Fate and Transport of fertiliser nitrogen under spring barley cultivation on contrasting soils

A thesis submitted for

The Degree of Doctor of Philosophy

School of Human and Environmental Sciences –
Department of Geography and Environmental Science

University of Reading

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Declaration of original authorship

I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged

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November 2016

Abstract

Mineral nitrogen (N) fertiliser inputs are essential for achieving high crop yields in agricultural production systems and can help to drive farm profitability. However, when N fertiliser is applied to soil it can be lost to the environment and have negative consequences. Such losses include nitrous oxide (N_2O) emissions, ammonia (NH_3) emissions and nitrate (NO_3^-) leaching to waterways. This loss of N fertiliser also represents a substantial economic loss of N from the farm.

The dominant N fertiliser source used on arable farms in Ireland is calcium ammonium nitrate (CAN) which, in environmental terms, principally contributes to N_2O emissions and NO_3^- leaching. Switching from CAN to urea has the potential to reduce these N loss pathways, but can result in substantially higher NH_3 emissions. Nitrogen stabilisers are compounds that can be added to N fertilisers to reduce these N losses.

There are two main types of N stabilisers currently available: urease inhibitors and nitrification inhibitors. Urease inhibitors are used to regulate urea fertiliser hydrolysis and to reduce NH_3 emissions and nitrification inhibitors are used to regulate the soil NO_3^- pool and to reduce N_2O emissions and NO_3^- leaching. The urease inhibitor used in this study was N-(n-butyl) thiophosphoric triamide (NBPT) and the nitrification inhibitor used was dicyandiamide (DCD). An additional N fertiliser formulation, urea + the maleic – itaconic co-polymer (MICO), was added in 2014. Two field sites cropped with spring barley were established in 2013 and the overall study was conducted for three years. Nitrous oxide emissions, NH_3 emissions, NO_3^- leaching and grain yield and N uptake were measured. The N fertilisers evaluated were CAN, urea, urea + NBPT, urea + DCD and urea + NBPT + DCD and Urea + MICO in 2014.

Results showed that N_2O emissions were low (over 50% lower than the IPCC default emission factor of 1%) regardless of the N fertilisers used but using the N stabilisers NBPT and DCD reduced emissions by up to 62%. There was no significant effect ($P>0.05$) of fertiliser formulation on NO_3^- leaching but there was a significant effect ($P<0.05$) on NH_3 emissions with urea + NBPT reducing emissions compared to urea. There was no significant effect ($P>0.05$) of fertiliser formulation on spring barley grain yield but there was significantly lower N uptake with urea compared to CAN. Using urea + NBPT had similar N uptake levels to CAN.

Overall this study showed that switching N fertiliser source from CAN to urea stabilised with the urease inhibitor NBPT can reduce environmental N losses and increase fertiliser N use efficiency (fNUE). This provides farmers with options to increase the environmental and economic sustainability of their arable farming systems while maintaining crop yields and quality.

Keywords: Nitrogen; N stabilisers; N fertilisers; urease inhibitor; nitrification inhibitor; nitrous oxide; ammonia; nitrate; grain yield;

Project Information

Funding for this project was provided by Irelands Department of Agriculture, Food and the Marine through the Sustainable Use and Disaggregated Emissions of Nitrogen (SUDEN) (Grant No. 11/S/138) and the Agricultural Greenhouse Gas Research Initiative - Ireland (AGRI-I) (Grant No. 10/RD/SC/716) and also through the Teagasc Walsh Fellowship Scheme. The experimental field sites were set up in Co. Wexford, Ireland and experimental work was conducted at the Teagasc, Johnstown Castle, Research Centre. PhD supervision was provided through the University of Reading by Associate Professor Dr. Liz Shaw and through Teagasc by Dr. David Wall, Dr. Karl Richards, Dr. Gary Lanigan, Dr. Richie Hackett and Dr. Patrick Forrestal. Results of this project have been presented in the following publications and a full list of publications and presentations is shown in appendix A:

2016

- Roche, L., Forrestal, P.J., Lanigan, G.J., Richards, K.G., Shaw, L.J. and Wall, D.P., 2016. Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley. Agriculture, Ecosystems & Environment, 233, pp.229-237.

- Roche, L., Forrestal, P.J., Hackett, R., Lanigan, G.J., Richards, K.G., Shaw, L.J., Wall, D.P., 2016. How does urea and protected urea compare to CAN for spring barley production. National Soil Fertility Conference, Kilkenny 2016. Efficient fertilizer use for tillage crops pp 10 – 11.

- Roche, L., Lanigan, G.J., Richards, K.G., Wall, D.P. 2016. Nitrogen fertilizer selection for cereal crops – balancing agronomic and environmental goals. TResearch Spring Issue. Volume 11, Number 1, Spring 2016 pp 8 – 9 ISSN 1649 – 8917.

2015

- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Hackett, R., Wall, D.P. 2014. Selecting nitrogen fertiliser sources for improved yield and reduced gaseous emissions in spring barley production systems. RDS gold medal for best oral presentation, Teagasc Walsh Fellowship Seminar annual meeting, pp 7,RDS, Dublin, November 2015.

- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P. 2015. Evaluating the effect of fertiliser nitrogen type on grain yield in spring malting barley. Agricultural research Forum, Tullamore, Co. Offaly March 2015, pp. 3.

2014

- Roche, L., Richards, K.G., Forrestal, P.J., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P. 2014. Evaluating the effect of N fertiliser type on nitrous oxide emissions from spring barley. Agricultural Research Forum, Tullamore, Co.Offaly 10th and 11th March.pp 45.

- Roche, L., Richards, K.G., Forrestal, P.J., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P. 2014. Reducing nitrous oxide emissions from spring barley in Ireland. 18th Nitrogen Workshop, Portugal 30th June – 3rd July 2014.pp 497-499.

Acknowledgements

Firstly I would like to thank my supervisors for providing me with this PhD opportunity to conduct research on an interesting and important subject area. I would like to express my deepest gratitude to Dr. David Wall for his support and encouragement throughout the past four years. I would also like to thank the rest of the supervisory team Dr. Karl Richards, Dr. Gary Lanigan, Dr. Patrick Forrestal, Dr. Richie Hackett and Dr. Liz Shaw for their input and advice during the course of this research and keeping me focused to stay on track. I would also like to sincerely acknowledge Jim Grant for all his help with statistical analysis.

I would like to acknowledge the Department of Agriculture, Food and the Marine in Ireland and the Teagasc Walsh Fellowship Scheme for funding this research.

I would sincerely like to thank the field, lab and farm staff at Johnstown Castle, without whom, this work would not have been possible. To Chris Maddock for all his help in the field and in the lab carrying around N_2O chambers and taking and extracting hundreds of soil samples and for his constant help and support, to John Murphy for ongoing help and support in the field and lab. To Cathal Somers for analysing over 10000 gas samples and for all his gas advice along the way and to Denis Brennan and Maria Radford for their help with analysis, and advice and support which I will continue to appreciate now that we share an office! I would like to thank Carmel O Connor for analysis of soil samples for LECO and for all her help and advice, to Teresa Cowman and Sean Colfer for all their help with sorting and analysing soil and crop samples, and to Linda - Maloney Finn for her advice and support along the way. I would also like to thank John Corish for his help with ordering equipment and supplies and to Miriam McGuire for keeping us stocked with glassware for KCL extractions! I would like to extend my gratitude to Dr. Anna Fenelon for help in the lab, last minute ordering, student help and always having an open door for

help and advice when needed! I would also like to thank Sarah Lacey for support and encouragement and always having a smile to brighten up the day. I would also like to acknowledge the agricultural catchments programme for providing weather data for the MT field site and to Oliver Shine and Per - Erik Mellander for helping me with many queries. Lastly, I would like to thank all the interns and students that have helped over the last few years with any aspect of lab or field work.

I would like to thank Rioch Fox, Nicky Hayes, Brendan Connick, Paddy Hayes, Pat Donnelly and Donal Doyle for help getting the field equipment installed, fixing equipment when it broke down and for advice and support whenever it was needed, to the Oakpark staff Brendan, JP and Kieran for help with harvesting and crop sample analysis and also to James Masterson for allowing us access to the field over the last 4 years. Thanks to all my Johnstown friends and Walsh Fellows for making this experience a memorable and unforgettable journey - to my former housemates – Brian, Ian and Noeleen and to all the rest Philip, Gemma, Sara, Sophie, Noeleen, Fran, Joanne, Aaron, Ian T. Hannah, Lilian, Sarah, Eamon, Nicola, Andrea, Eoin, Mairead, Orlaith, Dominika, William, Simon, Eddy and last but not least my partner in crime and office buddy Mary – to the Walsh fellows, a great bunch of lads!

And lastly I would like to acknowledge my close circle of friends and family who have been there, and provided me with outlets unrelated to the PhD; Debbie, Jamie-Lee, Sarah, Emily, Aine, Mary, Tanya, Sabrina and Kim. To my parents, Matthew and Anne who have always supported and encouraged me, and without whom I would never have got this far in my education. I am truly grateful and I promise I’ll give up being a student now and enter the real world!

Publications arising from this thesis

Peer-reviewed

Chapter 4

Roche, L., Forrestal, P.J., Lanigan, G.J., Richards, K.G., Shaw, L.J. and Wall, D.P., 2016. Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley. Agriculture, Ecosystems & Environment, 233, pp.229-237.

Planned submission for peer-review

Chapter 5

Roche, L., Richards, K.G., Forrestal., P.J., Lanigan, G.J., Shaw, L.J., Wall, D.P., 2016. The effect of N fertiliser formulation on nitrate leaching from spring barley. The Journal of Agricultural Science.

Chapter 7

Roche, L., Hackett, R., Forrestal., P.J., Lanigan, G.J., Richards, K.G., Shaw, L.J., Wall, D.P., 2016. Effect of N fertiliser formulation on spring barley grain yield and crop N uptake. Agronomy Journal.

Acronyms and abbreviations

AN	Ammonium nitrate
AOB	Ammonia oxidising bacteria
AMO	Ammonia monooxygenase
Ca	Calcium
CAN	Calcium ammonium nitrate
CO_2	Carbon Dioxide
C:N	Carbon to nitrogen ratio
CH_4	Methane
DAFM	Department of Agriculture Food and Marine
DCD	Dicyandiamide
DON	Dissolved organic nitrogen
DMPP	Dimethylpyrazole phosphate
ECD	Electron Capture Detector
EC	European Commission
EF	Emission factor
EPA	Environment Protection Agency
ETS	Emissions Trading Scheme
EU	European Union
$_f$NUE	Fertiliser Nitrogen Use efficiency
FH2020	Food Harvest 2020
FW2025	Food Wise 2025
GAP	Good agricultural practices for protection of waters
GC	Gas Chromatograph
GHG	Greenhouse Gas
GWP	Global Warming Potential
GWC	Gravimetric Water Content
GS	Growth Stage
HAO	Hydroxylamine oxidoreductase
H	Hydrogen
H_2O	Water
HFC	Hydroflurocarbon
IPCC	Intergovernmental Panel on Climate Change

IEA	International Energy Agency
JC	Johnstown Castle
K	Potassium
KCl	Potassium Chloride
LOI	Loss on Ignition
MDF	Minimum Detectable Flux
MICO	Maleic-itaconic acid Co-polymer
MIT	Mineralisation-Immobilisation Turnover
Mg	Magnesium
MT	Marshalstown
N	Nitrogen
N_2	Dinitrogen
NAP	Nitrates Action Plan
N_2O	Nitrous oxide
NH_3	Ammonia
NH_2OH	Hydroxylamine
NEC	National Emission Ceilings
NO	Nitric oxide
NO_3^-	Nitrate
NO_2^-	Nitrite
NOx	Nitrogen Oxides
$(NH_2)_2CO$	Urea
NH_3	Ammonia
NH_4^+	Ammonium
$(NH_4)_2CO_3$	Ammonium carbonate
NBPT	n-butyl thiophosphoric triamide
ND	Nitrates Directive
Nr	Reactive nitrogen
NXR	Nitrite oxidoreductase
O_2	Oxygen
OECD	Office of Economic Cooperation and Development
P	Phosphorus
PET	Potential evapotranspiration

PFC	perfluorcarbon
S	Sulphur
SF_6	Sulphur hexafluoride
SO_2	Sulphur Dioxide
SOC	Soil organic Carbon
SOM	Soil Organic Matter
TON	Total oxidised nitrogen
TN	Total N
UNECE	United Nations Commission for Europe
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention on Climate Change
UK	United Kingdom
US	United States
VOCs	Volatile Organic Compounds
VWC	Volumetric Water Content
WFD	Water Framework Directive
WHO	World Health Organisation
WFPS	Water Filled Pore Space
WMO	World Meteorological Organisation

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Equation 5.2 Calculation for cumulative N leached from each lysimeter (kg ha^{-1})

Chapter 1 - General Introduction

Nitrogen (N) is a naturally occurring chemical element that is essential for all life on earth. The atmosphere contains 78% N in the form of dinitrogen gas (N_2) but this must be first 'fixed' before it can be made plant available. Synthetic N fertilisers are manufactured through the Haber-Bosch process to support crop and food production and worldwide N fertiliser use is approximately 100 Tg N yr^{-1}(Erisman et al., 2008). In 2008 N fertilisers were responsible for feeding approximately 44% of the world's population (Erisman et al., 2008). As a result, there is a consistent demand for synthetic N fertiliser to support crop production in order to feed a growing population. However, this can result in negative environmental impacts (Gruber and Galloway, 2008). Environmental losses of N include emissions of nitrous oxide (N_2O) which contribute to global warming, emissions of ammonia (NH_3), which can contribute to eutrophication and acidification and nitrate (NO_3^-) leaching to ground and surface waters which can potentially lead to eutrophication and to health risks in drinking water (Cameron et al., 2013). Losses of NO_3^- and NH_3 can also contribute to indirect N_2O emissions. Finally, nitrogen can also be lost as benign N_2 gas which is returned back to the atmosphere completing the N cycle.

These environmental N losses contribute to low fertiliser N use efficiency ($_f$NUE). Fertiliser N use efficiency here is described as the N recovered in the above ground biomass at harvest as a percentage of the N applied. Fertiliser NUE is usually low with studies reporting efficiencies of less than 50% of the N applied (Chien et al., 2009). Dobermann (2005) showed an average of 51% $_f$NUE, from over 800 experiments, in the above ground biomass of cereal crops. This low NUE coupled with the environmental losses of N represents an economic loss from the farm.

The main source of N used in Irish tillage systems is synthetic N fertilisers. The dominant straight N source used for arable farms in Ireland is calcium ammonium nitrate (CAN)

which contains 27% N. Of this N, 50% is in the form of NO_3^- and 50 % is in the form of ammonium (NH_4^+). The NO_3^- can be easily leached from the system or lost as N_2O gas through the process of denitrification (Cameron et al., 2013) and the NH_4^+ can be rapidly converted to NO_3^- and then lost through the same N loss pathways (Norton, 2008). Changing N fertiliser source from CAN to urea could potentially reduce N_2O emissions and NO_3^- leaching as urea-N must go through two conversion steps before it is transformed to NO_3^-. However N can be lost from urea as NH_3 during the process of urea hydrolysis and subsequent volatilisation of the produced NH_3 (Cameron et al., 2013). Previous studies have shown reduced cereal grain yields using urea compared to CAN due to N lost as NH_3 (Devine and Holmes, 1963; Gately, 1994; Conry, 1997a).

Nitrogen stabilisers (also known as inhibitors) are compounds that can be added to N fertiliser to reduce these N loss pathways. There are two main types of N stabilisers, classified as urease inhibitors and nitrification inhibitors. A urease inhibitor slows down the process of urea hydrolysis thereby reducing ammonia volatilisation. A nitrification inhibitor slows down the nitrification process thereby reducing N_2O losses during the ammonia oxidation step of nitrification and also reducing the size of the soil NO_3^- pool and potentially reducing N_2O losses through denitrification and NO_3^- leaching. Both of these N stabilisers have been shown to reduce N losses from agricultural soils (Watson et al., 1994; McTaggart et al., 1997; Di and Cameron, 2002a; Zaman and Blennerhassett, 2010; Sanz-Cobena et al., 2012; Misselbrook et al., 2014; Forrestal et al., 2015). Nitrogen stabilisers have also been shown to improve $_f$NUE in cropping systems (Abalos et al., 2014; Alonso-Ayuso et al., 2016; Herrera et al., 2016).

There is limited research on N stabilisers used in Ireland with no studies evaluating multiple environmental N losses (including N_2O, NH_3 and NO_3^-) simultaneously with

agronomic production aspects on spring barley and so the overall objectives in this thesis were:

1. To quantify the effect of N fertiliser formulation including N stabilisers on N_2O emissions
2. To quantify the effect of N fertiliser formulation including N stabilisers on NO_3^- leaching
3. To assess the effect of N fertiliser formulation including N stabilisers on NH_3 emissions
4. To quantify the effect of N fertiliser formulation including N stabilisers on spring barley grain yield and N uptake.

Two field experiments were established in Co. Wexford on two sites with contrasting soil types: Marshalstown (MT) and Johnstown Castle (JC). At both field sites the experiment included measurements of NO_3^- leaching using lysimeters, NH_3 concentration measurement using passive shuttles and agronomy measurements of grain yield and crop N uptake. At the MT field site measurements of N_2O using static chambers were also taken over a two-year period. Fertiliser formulations consisted of CAN, urea, urea + the urease inhibitor NBPT, urea + the nitrification inhibitor DCD and urea with both of these inhibitors. In 2014 and 2015 urea + the maleic – itaconic co-polymer (MICO) was added to the experimental design and evaluated for N_2O emissions, grain yield and N uptake.

A review of the literature identifies the gaps in existing knowledge and establishes the research objectives for this thesis in **Chapter 2**. In **Chapter 3** general materials and methods for the overall study and experimental design are described. The impacts of fertiliser nitrogen formulation and N stabilisers on N_2O emissions are discussed in **Chapter 4**, NO_3^- leaching in **Chapter 5**, NH_3 emissions in **Chapter 6** and spring barley

grain yield and N uptake in **Chapter 7**. **Chapter 8** incorporates results from all chapters and discusses the overall conclusions from this PhD study with recommendations for future research.

Chapter 2 - Literature Review

2.1 Overview

This introductory chapter outlines the implications of greenhouse gases (GHGs) in the atmosphere at global and national scale and shows Ireland's GHG emissions by sector highlighting that agriculture is the main contributor to national greenhouse gas emissions. This is followed by an overview of the soil N cycle covering N transformations and the main N loss pathways of volatilisation, nitrification, denitrification and leaching. Current N fertiliser usage in Ireland is discussed followed by using N stabilisers for reducing environmental N losses.

The N recommendation system in Ireland for spring barley is covered with an overall concluding section on how to reduce GHGs from spring cereal production systems such as spring barley in Ireland. This chapter concludes by outlining the objectives and hypotheses tested in the current research study and provides an outline for the proceeding chapters in this thesis.

2.2 Implications of increased levels of greenhouse gases in the atmosphere

Climate change is a global concern that is driven by increased levels of greenhouse gases (GHGs) in the atmosphere. The average global surface temperature has increased by 1°C since the late 19th century as a result of increased GHG concentrations in the atmosphere (Stocker et al., 2014). Greenhouse gases absorb infrared heat in the atmosphere and emit radiation which warms the earth. The three main GHGs of concern are carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). The concentration of GHGs in the atmosphere has increased since the beginning of the industrial revolution primarily due to human activities. From pre-industrial times (1750 – 1800) to 1990, concentrations of GHGs have increased by 26% for CO_2, 115% for CH_4 and 8% for N_2O (Watson et al.,

1990a). In 2010 global anthropogenic GHG emissions were 35% higher than 1990 and were approximately 46 billion metric tons of CO_2 equivalents (U.S. EPA., 2016). During this time period of 1990 - 2010 CO_2 emissions increased by 42%, N_2O emissions increased by 9% and CH_4 emissions increased by 15%. These gases have different lifetimes in the atmosphere with CO_2 between 50 and 200 years, CH_4 approximately 10 years and N_2O approximately 150 years (Watson et al., 1990a). This means that even if the quantity of GHGs being produced is reduced immediately it will take decades, even centuries before the atmospheric concentration of these gases is reduced overall, highlighting the importance of developing mitigation options and reducing GHGs for future generations.

The United Nations Framework Convention on Climate Change (UNFCCC) is an international environmental treaty with a goal of stabilising GHG emissions in the atmosphere. It was adopted at the 'Rio Earth Summit' in 1992 and entered into force on 21st March 1994. Industrialised countries were considered to produce the most GHGs and were expected to do the most to reduce emissions. These countries are known as Annex 1 countries and Ireland is included in this list. The Kyoto Protocol is what commits these Annex 1 countries to act and stabilise GHGs in the atmosphere; the convention only encourages parties to do so. The Kyoto Protocol was adopted in Kyoto, Japan on 11th December 1997. It set binding emission reduction targets for 37 industrialised countries and the European Commission (EC) including Ireland. The first commitment period was from 2008 – 2012 and the second commitment period, governed by the EU climate and energy package 2020 (406/2009/EC), started on January 1st 2013 and runs to 2020. The EU climate and Energy Framework which builds on the climate and energy package has set targets to reduce GHG emissions by 30% below 1990 levels by the year 2030.

The UNFCCC requires parties to the convention to publish and update national inventories of anthropogenic emissions of these and other GHGs but it is the Intergovernmental Panel on Climate Change (IPCC) through the Office of Economic Cooperation and Development (OECD) and International Energy Agency (IEA) which coordinates the development of these methodologies for national inventories (Mosier et al., 1998). The IPCC was set up in 1988 by the World Meteorological Organization (WMO) and United Nations Environment Programme (UNEP) to provide policymakers with regular assessments of climate change and mitigation options.

In the 1990s attempts were made to define global N_2O budgets and Mosier et al. (1998) suggested that by considering only direct N_2O emissions from agricultural fields fertilized by synthetic N fertilizer, N_2O sources were being underestimated. Indirect N_2O emissions include nitrate (NO_3^-) leaching and ammonia (NH_3) volatilisation. The IPCC methodology requires parties to account for direct and indirect N_2O emissions as indirect losses of N may later lead to N_2O losses from denitrification in other ecosystems (Mosier et al., 1998).

2.2.1 Irelands GHG emissions

As a party to the UNFCCC and the Kyoto Protocol, Ireland is committed to developing and publishing national inventories of GHGs. The Environmental Protection Agency (EPA) compiles Ireland's national GHG emission inventory report each year and this is submitted to the European Commission (EC) on 15th January and to the UNFCCC on 15th April each year. Emissions data for the main GHGs N_2O, CH_4 and CO_2 are included in this inventory as well as other gases (Hydrofluorocarbons (HFCs), Perflurocarbons (PFCs), Sulphur Hexaafluoride (SF_6) and nitrogen Trifluoride (NF_3)) and GHG emissions are divided into six sectors which are Energy, Residential, Industry & Commercial, Agriculture, Transport and Waste. The most recent GHG inventory report covers 1990 – 2014 and this shows that

agriculture accounts for the highest proportion of emissions with 37.1% in 1990 and 33.1% in 2014 (Figure 2.1) (EPA, 2016).

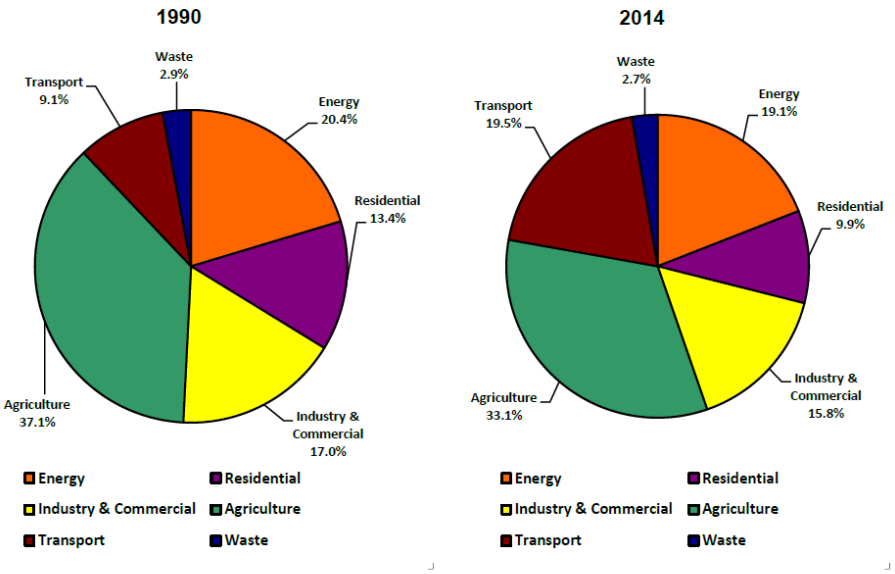

Figure 2.1 Irelands greenhouse gas emissions by sector in 1990 and in 2014 (EPA, 2016)

Globally agriculture is the 2nd largest source of GHG emissions accounting for 13% of total emissions in 2010 (U.S. EPA, 2016). Under the Kyoto Protocol, Ireland was required to reduce GHG emissions to 13% above 1990 levels which were 62.836 million tonnes of carbon dioxide equivalent (CO_2 eq) compared to 55.607 CO_2 eq in 1990. In 2012 Ireland had surpassed this target and was 5.68 MT CO_2 eq below the Kyoto limit excluding the EU emissions trading scheme (ETS) and forest sinks. The second commitment period is running from 2013 – 2020 and according to the guidelines of this period, Ireland must reduce GHGs to 20% below 1990 levels (EC, 2016).

Total agricultural emissions in Ireland are expected to increase by 12% by 2020, and the contribution of agriculture to non-ETS sector emissions is projected to increase to almost 50% by 2020 (EPA, 2013). The climate and energy framework which builds on the climate

and energy package has set binding targets for the EU territory to reduce GHG emissions by 40% by 2030. Thus, these projections show the importance of developing GHG mitigation options in order to achieve 2020 and 2030 reduction targets. The baseline for GHG emissions is 1990 as this is the first year that GHG emission estimates were generated. In Figure 2.2, emissions trends from 1990 – 2014 are shown showing an overall reduction in emissions from the agriculture sector since 1990.

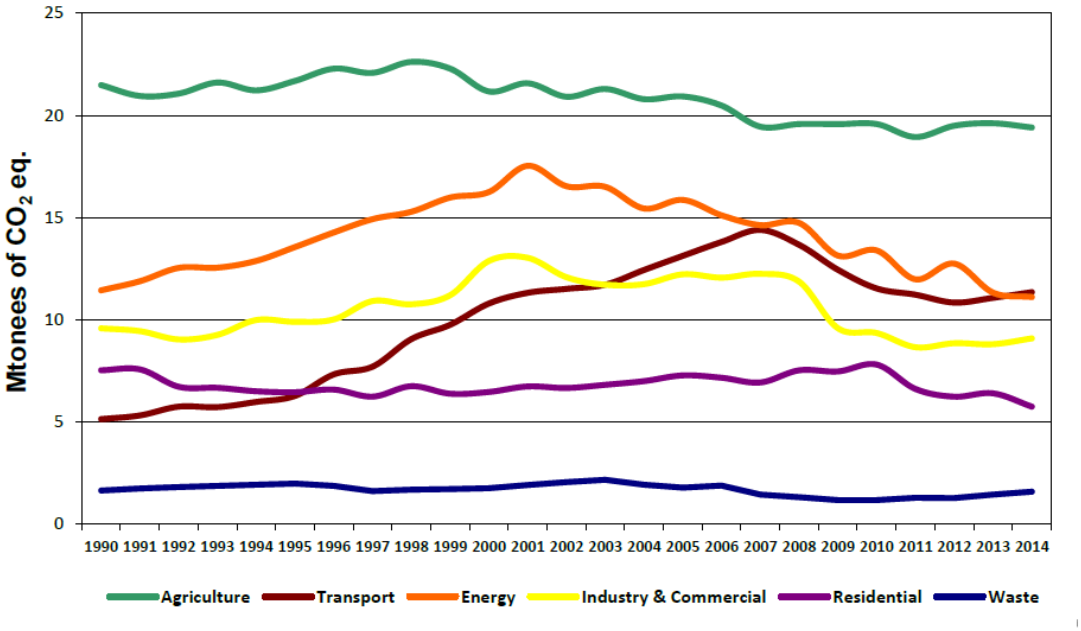

Figure 2.2 Trends in greenhouse gas emissions in Ireland from 1990 – 2014 (EPA, 2016)

Emissions in agriculture reached a peak in 1998 and have been decreasing below 1990 levels since 2002. In 2014 emissions were 7.5% below 1990 levels (EPA, 2016). Although there is a downward trend for GHG emissions from agriculture, mitigation options are still needed to further reduce GHG emissions in order to achieve 2020 and 2030 reduction targets. As well as environmental N loss reduction targets, Ireland has published documents on production targets for agriculture. Food Harvest 2020 (FH 2020) (DAFM, 2010) was launched in 2010 and sets clear, ambitious growth targets for the agriculture

sector to be achieved by 2020. Food Wise 2025 (FW 2025) (DAFM, 2015) is a strategy for growing the agri-food, forestry and fisheries sector for the next decade. One of the main aims of FH 2020 is to increase the value of primary output in the agriculture, fisheries and forestry sector by €1.5 billion which is a 33% increase on the 2007 – 2009 average (DAFM, 2010). Following on from this, FW 2025 aims to increase the value of primary production by 65% to almost €10 billion. To achieve these national agricultural production targets, an increase in N fertiliser use will be necessary and so it is essential to consider mitigation options for reducing GHGs.

The current study is on arable land cropped with spring barley and the biggest contributor to GHGs from arable land is N_2O being emitted from the application of N fertilisers to soils. Globally N_2O emissions from the application of synthetic fertilisers accounts for 12.6% of global GHG emissions (FAOSTAT, 2016a) and in Ireland N application accounts for 22% of total agricultural emissions (EPA, 2013).

2.3 Nitrous Oxide (N_2O)

Nitrous oxide is a potent GHG with a global warming potential (GWP) 265 times that of CO_2 on a 100 year time frame (Myhre et al., 2013). Global warming potential is a relative measure of how much heat a certain mass of a GHG traps in the atmosphere compared to how much heat is trapped by the same mass of CO_2. This means that every gram of N_2O emitted is equivalent to 265 grams of CO_2. Nitrous oxide is one of the six targeted GHGs that must be reduced under the Kyoto Protocol and one of the main sources of this is from the application of N fertilisers to agricultural land (Davidson, 2009). Nitrous oxide is a naturally occurring gas that is produced in soils through the microbial processes of nitrification and denitrification, but there has been an increase in its concentration over the

last 200 years due to an increase in anthropogenic activities. The atmospheric concentration of N_2O is continuously increasing at an average rate of 0.75 parts per billion (ppb) yr^{-1} since the 1970s (IPCC, 2014) and in 2011 its concentration reached 324.2 ppb which was a 20% increase on 1750 levels.

The Environmental Protection Agency (EPA) in Ireland estimates annual N_2O emissions to the atmosphere for the national inventory using a default emission factor (EF) from the Intergovernmental Panel on Climate Change (IPCC). An EF is defined as the percentage of N_2O emitted as a proportion of the N applied. The IPCC has a three Tier approach for estimating N_2O emissions. The Tier 1 methodology is a crude measurement that does not take into account different crops or soil types, climatic conditions or management practices (de Klein et al., 2006), all of which have been demonstrated to affect emissions (Dobbie et al., 1999; Dobbie and Smith, 2003a, 2003b; Lesschen et al, 2011). Countries with sufficient data to show that default EFs are not appropriate for their country can use Tier 2 or Tier 3 approaches. The formula for calculating Tier 1 emissions can be seen in Equation 2.1.

$$N_2O_{Direct}\text{-}N = N_2O\text{-}N_{Ninputs} + N_2O\text{-}N_{os} + N_2O\text{-}N_{prp}$$

Equation 2.1 Formula for calculating Tier 1 N_2O emissions

Where:

N_2O_{Direct}-N = annual direct N_2O-N emissions from N inputs to managed soils

$N_2O\text{-}N_{Ninputs}$ = annual direct N_2O-N emissions from N inputs to managed soils

$N_2O\text{-}N_{os}$ = annual direct N_2O-N emissions from managed organic soils

$N_2O\text{-}N_{prp}$ = annual direct N_2O-N emissions from urine and dung

In order to use Tier 2 or Tier 3 methodologies, rigorously documented country specific EFs are needed. Further details of these tiered methodologies and equations are explained in de Klein et al. (2006). The IPCC default EF used in Ireland for direct N_2O emissions from synthetic N fertilisers is 1% under managed soils (IPCC, 2006). This means that for every 100 kg N fertiliser applied to soil it is estimated that 1 kg N is emitted to the atmosphere as N_2O.

The collection of more informed data would allow us to use the Tier 2 methodology and produce more detailed and accurate EFs specific for soil type and crop type (IPCC, 2006). Subsequently this data could also be incorporated into the development of new N fertiliser recommendations in Ireland, therefore ensuring continued adherence to reducing GHG emissions in line with the 2020 targets. This current study was conducted on spring barley which is an important cereal crop in Ireland. One of the main GHGs from arable land is N_2O emitted from the application of N fertilisers to land but limited information exists on the gaseous N losses from its production in Ireland.

2.4 Legislation for reducing N losses to the environment

As well as GHG reductions, there are other obligations Ireland has to comply with in order to minimise or reduce N losses to the environment. There are five particularly important directives which are important for agriculture and nutrient use in Ireland:

- The Water Framework Directive (WFD) (2000/60/EC) with a requirement for all European ground and surface water bodies to reach ‘good ecological status’ by 2015, and now 2021.

- The Nitrates Directive (91/676/EEC) which aims to protect water against agricultural sources of NO_3^- pollution (linked to the WFD through national NO_3^- management programmes)
- The Convention of Long Range Transboundary Air Pollution (CLRTAP, 1979) and
- The Gothenburg Protocol adopted by the United Nations Economic Commission for Europe (UNECE) (1999) to abate acidification, eutrophication and ground level ozone.
- The above two are linked to the National Ceilings Directive (2001/81/EC) on reducing sulphur dioxide (SO_2), oxides of nitrogen (NO_x), volatile organic compounds (VOC) and ammonia (NH_3) emissions.

All of these directives have one common aim of managing N losses to the atmosphere, water and land. A high proportion (80%) of Ireland's land-use is engaged in agricultural production and N is used in order to achieve high yields from crops but this N can be lost from the soil system and have negative environmental impacts. Agriculture is one of the main sources of pollution to rivers and lakes accounting for 53% in 2010 – 2012 (Byrne and Fanning, 2015) and was responsible for 88% of N pollution to surface waters in 2010 – 2012. The Water Framework Directive (WFD) (2000/60/EC) legislation was introduced in the EU in December 2000 and its aims were to protect all waters including surface, ground and coastal and to achieve good water status by December 2015. For territories where water bodies have not achieved this target the next reporting period is 2021 under WFD. The EU Nitrates Directive (ND) (1991) forms an integral part of the WFD and its aims are to protect water quality from pollution from agricultural sources and to promote good farming practice. Under the Nitrates Directive each member state is required to prepare a national Nitrates Action Plan (NAP) which outlines rules for management and application of organic manures and inorganic fertilisers. Irelands first NAP was implemented in 2006

(SI, 378 of 2006). Member States are required to review NAPs at least every four years and Irelands most recent NAP was implemented in 2014 (SI, 31 of 2014) and will be reviewed for a fourth time in 2017. This NAP is known as the good agricultural practice for the protection of waters and constrains the use of N and phosphorus (P) fertilisers and defines maximum allowable limits for N and P. Member states are required to monitor compliance of the WFD and ND and where member states have breached these rules they will be subject to fines. At farm level non-compliance with the rules set out in the NAP will result in fines and the higher the breach in the rules, the higher the fine.

The Convention on Long-range Transboundary Air Pollution was the first international treaty to deal with air pollution and it entered into force in 1983 with the aim of reducing air pollutant emissions. This led onto the Gothenburg Protocol to abate acidification, eutrophication and ground-level ozone which entered into force in 1999. This sets national emission ceilings for 2010 for four air pollutants, sulphur (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and ammonia (NH_3). Parallel to the Gothenburg Protocol, EU member states set upper limits for these four air pollutants under the National Emission Ceilings Directive (NEC). The upper limit for NH_3 emissions in this is 116 Kt per year after 2010. Changes proposed to the NEC will require NH_3 reduction targets of 5% below 2005 levels by 2030 (EC, 2013).

In Ireland, agriculture is responsible for 99% of NH_3 emissions (EPA, 2015), 81% of N_2O emissions and 86% of CH_4 emissions to the atmosphere. Although total GHG emissions from agriculture are on a downward trend, there is a still a long way to go to meet 2020 and 2030 reduction targets. Fertiliser sales are expected to increase by 16% by 2020 (EPA, 2013) which could lead to an increase in N_2O or NH_3 emissions so further mitigation

efforts are needed to keep on track and ensure continued adherence to 2020 and 2030 reduction targets.

2.5 Nitrogen as a global concern

Nitrogen is fundamental to agriculture for crop production to feed a growing population. Many studies have shown that agricultural N losses have environmental impacts mainly through gaseous emissions to the atmosphere in the form of N_2O (Harty et al., 2016; Roche et al., 2016) or NH_3 emissions (Forrestal et al., 2015) and also through NO_3^- leaching to groundwater (Hooker et al., 2008). These losses have also shown to have ecological effects (Vitousek et al., 1997) and effects on human health (Knobeloch et al., 2000; Ward et al., 2005). The global N cycle is changing anthropogenically through the combustion of fossil fuels, production of N fertilisers, and cultivation of N-fixing legumes (Galloway et al., 1995). These sources of change are causing an increase in the quantity of gaseous N in the atmosphere including increased levels of N_2O and NH_3. Nitrous oxide emissions have increased at a rate of 0.75 ppb yr^{-1} rising 20% since 1750 to 324 ppb (IPCC, 2014) and soils contribute substantially to this increase accounting for approximately 65 – 70% of emissions from terrestrial ecosystems (Brown et al., 2001). There have been numerous studies on mitigation options to reduce N_2O and NH_3 emissions (Kim et al., 2012; Rees et al., 2013; Forrestal et al., 2015; Hinton et al., 2015; Harty et al., 2016; Roche et al., 2016) but with expected population growth and increased N fertiliser use, further studies are needed on mitigation options of N_2O in order to meet 2020 and 2030 reduction targets while also meeting production targets set out in FW2025.

2.6 Nitrogen and the Soil Nitrogen Cycle

Nitrogen is an essential nutrient for all life on earth and is often the most limiting nutrient for plant growth. Nitrogen is a key component of amino acids which make up proteins and enzymes and are important for biological processes. The N content of most soils is approximately 0.1 – 0.6% in the top 10cm which represents approximately 2 – 12 t N ha^{-1} depending on soil type (Cameron et al., 2013). Nitrogen in soil is mostly in the form of organic N in organic matter and in mineral N forms of NH_4^+ and NO_3^- (Cameron et al., 2013). Soil organic matter (SOM) is composed of a continuum from fresh to progressively decomposing plant, microbial and faunal-derived debris and exudates, including the microbial biomass that is responsible for the primary decomposition of the exudate and detrital inputs. Approximately 95 to 98% of the total N in soils exists as an organic component of SOM with the remainder 2 - 5% consisting of mineral N (Whitehead, 1995; Brady and Weil, 2002) added to the soil as organic or inorganic N fertiliser and/or produced from the SOM by the mineralisation process (Explained in section 2.6.1). Soil organic N is the dominant N pool and in arable soils the surface layer of soil typically contains 2 - 6 t N ha^{-1} in organic matter (Powlson, 1993). Plants require N for growth and development, without which plants would be yellowish in colour, have stunted growth and develop thin stems (Brady and Weil, 2002). It is important to apply adequate N to crops for plant growth and development and to achieve optimum crop yields but oversupply of N can have negative effects causing excessive vegetative growth, weak and top-heavy stems and can cause lodging in cereal grains (Brady and Weil, 2002) as well as contributing to environmental N losses. Plants mainly take up N in the mineral forms of NH_4^+ and NO_3^- but some plants can use amino acids (Brady and Weil, 2002).

The atmosphere contains approximately 78% N in the form of dinitrogen (N_2) gas but this is unavailable to plants and must be first fixed before it can become available. Dinitrogen has a triple bond holding the two N atoms together as N_2 and requires high energy to break this bond such as that provided by the hydrolysis of ATP molecules in biological N fixation, lightning and more recently the Haber-Bosch process. Only plants that can form a symbiotic relationship with N-fixing bacteria can utilise N_2 from the atmosphere, and most food crops including cereals are not capable of this, therefore rely on N derived from mineralisation of SOM and N fertiliser inputs. Most crops require N fertiliser to provide adequate N for achieving optimum crop yields, as the N derived from SOM mineralisation is not adequate to achieve high yields (Evenson and Gollin, 2003). The transformation processes and losses of N from the soil system affect the availability of N for plants and transfer of N to the wider environment (Cameron et al., 2013) (Figure 2.3). The quantity of mineral N in soils can be estimated by the following equation:

$$N = N_p + N_b + N_f + N_{pr} + N_m - N_{pl} - N_g - N_i - N_l - N_e$$

Equation 2.2 N balance equation for the quantity of mineral N in the soil (adapted from Cameron et al., 2013).

Where p is N atmospheric inputs via precipitation and dry deposition, b is biological fixation, f is fertiliser, pr is plant residue returns to the soil, m is mineralisation, pl is plant uptake, g is gaseous losses, i is immobilisation, l is leaching loss and e is erosion and surface runoff.

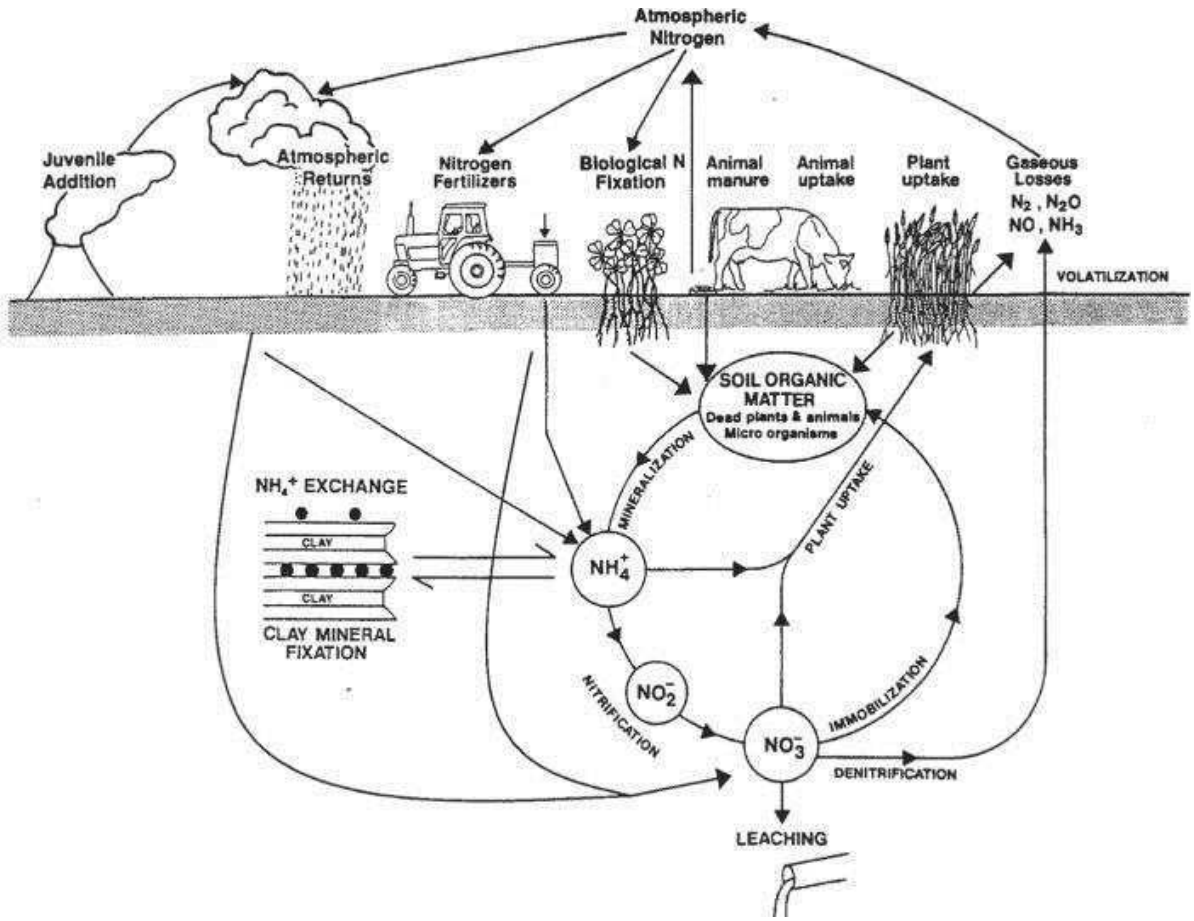

Figure 2.3 Soil/plant nitrogen cycle and transformations (Cameron et al., 2013)

There are many processes in the N cycle that take place in soil depending on the size, structure and activity of the soil microbial community, climate conditions and soil characteristics (Bremner, 1997). Nitrogen fixation converts gaseous N_2 into ammonium and can occur with leguminous plants such as clover forming a symbiotic relationship with microorganisms. N fixation can also occur with lightning where the energy in lightning can break the triple bonded N molecules which can then form a bond with oxygen (O_2) in the atmosphere and undergo oxidation and deposition to add N to the soil. Once N is in the soil system it can then undergo many transformations which can occur simultaneously including mineralisation, immobilisation, volatilisation, nitrification, denitrification and these processes are explained below. The main N losses in the soil N cycle are through

ammonia volatilisation, leaching and denitrification (Cameron et al., 2013) which are the main loss pathways that are discussed in this thesis.

2.6.1 Mineralisation and Immobilisation

Mineralisation is the conversion of organic N into inorganic N, i.e. mineral N which is plant available. Ammonification is the production of NH_4^+ through enzymatic processes that occurs as a final step of mineralisation (Myrold and Bottomley, 2008). Soil organic matter (SOM) is central to these two processes. The SOM pool contains a diverse mixture of complex organic constituents (Brady and Weil, 2002) and is estimated to contain approximately 150,000 million tonnes of N in global terrestrial ecosystems (Jenkinson, 1990). Arable soils cropped with cereals have an annual input of organic carbon into soil of approximately 1 - 2 t ha^{-1} which is about half of the organic carbon of a grassland soil (Jenkinson and Rayner, 1977). Over 95% of N found in soil is in the form of SOM which is unavailable to plants and these complex organic constituents must be broken down to simple inorganic compounds through mineralisation before they can be used by plants (McLaren and Cameron, 1996). Mineralisation accounts for the background supply of N in the soil and N mineralisation rates depend on temperature and soil moisture (Smith et al., 1977) and also texture and organic matter content (Herlihy, 1979). It is important to account for the background supply of N when developing N fertiliser management strategies as excess N addition could result in high levels of soil NO_3^- being produced which can be leached (Keeney and Cruse, 1991) or lost as nitrous oxide gas through denitrification.

The reverse process of mineralisation is immobilisation where N is converted from mineral N forms into organic N (Myrold and Bottomley, 2008). Mineralisation and immobilisation

occur simultaneously in soil and are mediated by the soil microbial population (Powlson, 1993). Mineralisation and immobilisation are opposing N transformation processes and determine the quantity of plant available N in soils that is derived from SOM. The term net N mineralisation is used to account for gross N mineralisation and gross N immobilisation turnover (MIT) (Luxhøi et al., 2006). Net N mineralisation can occur when SOM has a high N content with a low C:N ratio, typically <25:1 in agricultural soils, and in contrasting conditions net N immobilisation can occur (McLaren and Cameron, 1996)

2.6.2 Nitrification

Nitrification is a two-step oxidation process where a relatively immobile N-from, ammonium, is oxidised to a relatively mobile N-form, nitrate via nitrite. The first step is carried out by ammonia oxidising bacteria (AOB) such as *Nitrosomonas* and *Nitrosospira* spp. (Norton, 2008) and also ammonia oxidising archaea (AOA) (Leininger et al., 2006) where NH_4^+ is converted to NO_2^- (Equation 2.3). Ammonia oxidising archaea don't appear to be as important as AOB in N-rich agricultural soils (Di et al., 2009) and may be more dominant in more acidic soils with AOB being more dominant in neutral, alkaline and N-rich soils (Shen et al., 2012). The second step is the oxidation of nitrite to nitrate and is carried out by *Nitrobacter* and *Nitrosospira* (Equation 2.4) (Norton, 2008). There are no known bacteria with capabilities to oxidise NH_4^+ to NO_3^- (Hooper et al., 1997).

$$NH_3 + O_2 + 2H^+ + 2\,e^- \rightarrow NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4\,e^-$$

Equation 2.3 The first step of the nitrification process (Norton, 2008)

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2\ e^-$$

Equation 2.4 The second step of the nitrification process (Norton, 2008)

The conversion of NO_2^- to NO_3^- takes place quite quickly and therefore NO_2^- does not accumulate in the soil (Cameron et al., 2013). However, there are exceptions of this on some high pH soils (i.e. calcareous soils) combined with high concentrations of existing or applied NH_4^+-N which can result in an accumulation of NO_2^- (Shen et al., 2003; Norton, 2008). In order for the oxidation of ammonia to nitrite to take place two enzymes are required which are ammonia monooxygenase (AMO), which is a major protein found in all AOB and AOA, and hydroxylamine oxidoreductase (HAO) (Norton, 2008). Ammonia monoxygenase is predicted to contain at least three subunits which are AmoA, AmoB and AmoC. AmoA contains the active site of the enzyme which has been identified by the binding of acetylene to this submunit AmoA (Hyman and Arp, 1992). The oxidation of nitrite to nitrate is carried out in the presence of the enzyme nitrite-oxidoreductase (NXR) (Norton, 2008). Soil AOB are from the class *Betaproteobacteria* and further details on soil nitrifier communities are discussed in Norton (2008). Soil AOA are from the phylum Crenarchaeota and further details on AOA are discussed in Leininger et al. (2006).

Ammonia oxidising bacteria can produce N_2O during the oxidation of NH_4^+ to (hydroxylamine) NH_2OH and NH_2OH to NO_2^- (Figure 2.4) (Cameron et al., 2013) which occurs when the soil water filled pore space is below 60% (Bateman and Baggs, 2005). It has always been reported that denitrification was the main pathway for N_2O loss (denitrification losses explained in section 2.6.3) but nitrifier denitrification can be a major pathway when soil moisture conditions are sub-optimal for denitrification (Kool et al., 2011).

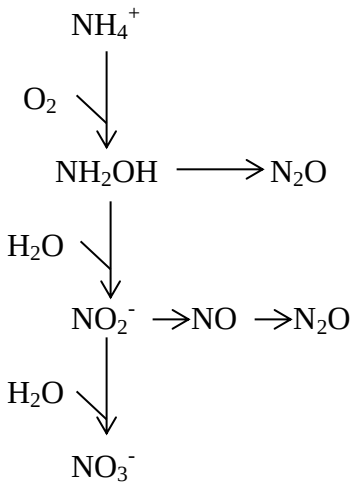

Figure 2.4 Production of N_2O during the oxidation of ammonium to nitrite (Cameron et al., 2013).

The availability of NH_4^+ and NH_3 is the main limiting factor for nitrification rates in agricultural soils as well as the resultant AOB and AOA population (Norton, 2008). Nitrification rates increase with increased rates of ammonium fertiliser additions in arable soils (Mendum et al., 1999). Oxygen availability, moisture content and temperature are environmental factors that affect nitrification (Norton, 2008) with nitrification rates decreasing with lower oxygen levels and higher moisture content.

Managing the nitrification process is important in agricultural soils for managing N losses including N_2O and NO_3^- leaching which can be lost as a result of the nitrification process. Nitrate is very mobile in soil and is more accessible for plant uptake compared to NH_4^+ but its ease of mobility makes it more vulnerable to losses from the soil system through leaching or denitrification producing N_2O emissions (Norton, 2008).

2.6.3 Denitrification

Denitrification is the reduction of NO_3^- into gaseous N forms which is mainly carried out by facultative anaerobic bacteria that use NO_3^- as an electron acceptor instead of O_2 in their respiratory metabolism in poorly drained soils. Nitrate is converted in a series of reduction reactions to NO_2^- to NO to N_2O and finally to N_2 (Saggar et al., 2013) (Figure 2.5). Denitrification can also be carried out by fungi but this has been shown to be more dominant in forest and grassland soils (Laughlin and Stevens, 2002) and in semiarid regions (Mclain and Martens, 2006). Denitrification is an important process in the N cycle as it is the major route that completes the N cycle and returns N back into the atmosphere as N_2. The reduction of NO_3^- to N_2 gas involves four reduction processes and each step requires a specific reducing enzyme, NO_3^- reductase, NO_2^- reductase, NO reductase and N_2O reductase (Figure 2.5).

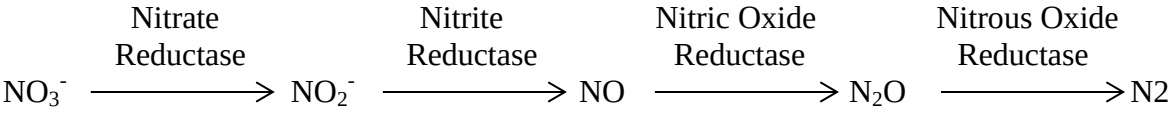

Figure 2.5 Reduction processes and enzymes within denitrification (Prosser, 2007)

Heterotrophic denitrification is an abundant soil process that occurs with an adequate soil carbon supply, a supply of NO_3^-, suitable soil temperature, anaerobic conditions (i.e. low oxygen levels) and denitrifying bacteria (Ryan, 1998). Most denitrifying bacteria possess all of the reducing enzymes, however there are some bacteria that do not and often N_2O is emitted into the atmosphere before it can be converted to N_2 (Haynes and Sherlock, 1986). Denitrifiers that lack one or more of the enzymes are said to be incomplete and most fungi and approximately one-third of sequenced bacterial denitrifiers lack N_2O reductase and so they emit N_2O as the final product (Saggar et al., 2013). Nitrous oxide can also be emitted

by organisms that do possess all reducing enzymes due to the 'hole in the pipe' model explained by Firestone and Davidson (1989). In the 'hole in the pipe' model, aeration and available carbon affect the distribution of denitrification products with increased aeration and reduced organic carbon restricting electron flow through the denitrification pathway and resulting in increased N_2O and NO losses (Firestone and Davidson, 1989; Coyne, 2008) (Figure 2.6).

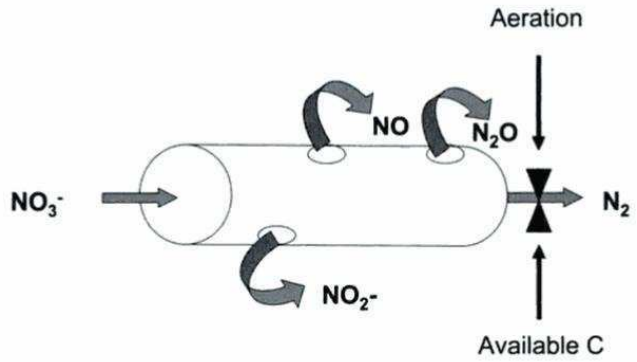

Figure 2.6 The influence of aeration and available C on the distribution of denitrification products – the 'Hole-In-The-Pipe' model. Increasing aeration and decreasing available C act to restrict electron flow through the denitrification pathway which leads to intermediate accumulation and loss (Coyne, 2008)

Nitrous oxide can also be produced through nitrifier denitrification and chemodenitrification (Wrage et al., 2001) and also coupled nitrification-denitrification (Butterbach-Bahl et al., 2013). Chemo-denitrification is a non-biological process and is the chemical decomposition of the intermediates from the oxidation of NH_4^+ to NO_2^- or of NO_2^- itself, with organic or inorganic compounds (Wrage et al., 2001). Coupled nitrification-denitrification is the production of nitrate by nitrite oxidisers, which is immediately denitrified in situ by denitrifiers (Butterbach-Bahl et al., 2013). Nitrifier-

denitrification is the oxidation of NH_3 to NO_2^- followed by the reduction of NO_2^- to NO, N_2O to N_2 and this is carried out by NH_3^- oxidisers (Wrage et al., 2001).

Soil and environmental conditions that affect denitrification include NO_3^- concentrations, carbon (C) availability, pH, temperature, moisture content and O_2 concentration (Saggar et al., 2014). Usually, biological denitrification is associated with anaerobic or waterlogged soil where the redox potential falls below 400 mV (Coyne, 2008). The factors affecting denitrification have been reviewed in previous studies (Haynes and Sherlock, 1986; Firestone and Davidson, 1989; Saggar et al., 2004; Coyne, 2008; Saggar et al., 2013) and examples of N_2O emissions with EFs ranging from 0.09% - 3.81% are shown in Table 2.1.

Table 2.1 A summary of nitrous oxide emissions from fertilised soils

N Input (Kg N ha^{-1} yr^{-1})	Soil Type	Crop Type	N source	N_2O EF (% of N applied)	Location	Reference
120	Sandy loam	Spring barley	AN	1.35%	Scotland	Hinton et al., 2015
120	Sandy loam	Spring Barley	Urea	0.64%	Scotland	Hinton et al., 2015
120	Sandy clay loam	Spring barley	AN	0.62%	England	Bell et al., 2015
120	Sandy clay loam	Spring barley	Urea	0.59%	England	Bell et al., 2015
132	Sandy loam	Winter barley	AN	0.5%	England	Dobbie and Smith 2003b
140	Sandy loam	Spring barley	CAN	0.63%	Ireland	Abdalla et al., 2010
150	Loam	Spring Barley	CAN	0.35%	Ireland	Roche et al., 2016
150	Loam	Spring Barley	Urea	0.27%	Ireland	Roche et al., 2016
160	Clay	Winter wheat	AN	0.23%	England	Smith et al., 2012
160	Clay	Winter wheat	Urea	0.60%	England	Smith et al., 2012
180	Loamy sand over sandy loam	Winter wheat	AN	0.17%	England	Bell et al., 2015
180	Loamy sand over sandy loam	Winter wheat	Urea	0.16%	England	Bell et al., 2015
180	Sandy clay loam	Winter wheat	Urea	0.37%	Scotland	Smith et al., 2012
180	Sandy clay loam	Winter wheat	CAN	0.25%	Scotland	Smith et al., 2012
190	Clay	Winter Wheat	AN	0.7%	England	Dobbie and Smith 2003b
200	Clay loam	Grassland	CAN	3.81%	Ireland	Harty et al., 2016
200	Clay loam	Grassland	Urea	0.3%	Ireland	Harty et al., 2016
200	Sandy loam	Grassland	CAN	0.58%	Ireland	Harty et al., 2016
200	Sandy loam	Grassland	Urea	0.1%	Ireland	Harty et al., 2016
240	Clay loam	Winter wheat	AN	0.09%	England	Bell et al., 2015
240	Clay loam	Winter wheat	Urea	0.11%	England	Bell et al., 2015

Studies have shown increases in denitrification rates with increased water content or reduced O_2 content (Bremner and Shaw, 1958; Pilot and Patrick, 1972; Ardakani et al., 1977). The presence of O_2 inhibits denitrifying enzyme activity and prevents new denitrifying enzymes from being synthesised (Payne, 1973). Smith and Tiedje (1979) showed that when soil becomes anaerobic the O_2 inhibition of denitrifying enzymes is removed and new denitrifying enzymes are synthesised, resulting in an increase in denitrification. As the soil moisture content increases, O_2 content decreases and so denitrification is likely to occur. Seitzinger et al. (2006) showed that denitrification will occur at O_2 concentrations below 0.2 mg O_2 L^{-1}. Bremner and Shaw (1958) showed that denitrification rates are slow in acid soils and temperatures of 2 - 5°C and are rapid in neutral and alkaline soils up to pH 8.6 and above 5°C. Moisture content had a bigger effect on denitrification rates showing that even in optimum pH and temperature, little denitrification takes place if the moisture content is less than 60% of the water-holding capacity of the soil. Denitrification is spatially variable with 'hot spots' of high denitrification levels compared to lower levels at the same sites. Christensen et al. (1990) showed high spatial variation of denitrification rates with rates ranging from 0.3 – 486 g N_2O-N ha^{-1} d^{-1}.

Nitrification and denitrification are important processes in agricultural soils as both can lead to losses of N as gaseous N_2O. With obligations to reduce GHG emissions it is important to develop N_2O mitigation options for agriculture. The N cycle can be considered metaphorically as a series of pipes which represent individual N transformation processes. Nitrification and denitrification are considered as processes that have holes in the metaphorical N transformation pipes through which gaseous N (N_2O, and also NO) can leak. The more N that flows through, the more leakage of gaseous N occurs; as with agricultural soils receiving N fertilisers, these leaks could be large. If N inputs are low and

there is low N mineralisation and high plant demand for N, then losses will be low (Davidson and Mosier, 2004). Gaseous emissions of N can also occur through ammonia volatilisation which can indirectly contribute to N_2O emissions. In general soils are considered a source of N_2O but some studies have shown potential for soils to act as sinks for N_2O (Chapuis-Lardy et al., 2007; Flechard et al., 2007).

2.6.4 Ammonia Volatilisation

Ammonia volatilisation is a complex chemical, physical and biological process that causes the loss of gaseous ammonia from the soil surface (Figure 2.3). There is an equilibrium in soil between NH_3 and NH_4^+ and the concentration of these are dependent on soil pH. In high pH conditions the OH^- ions drive the reaction to the right and NH_3 loss occurs (Equation 2.5) (Mills, 1974).

$$NH_4^+ + OH^- \longleftrightarrow NH_3 + H_2O$$

Equation 2.5 Equilibrium between NH_3 and NH_4^+ in soil (Cameron et al., 2013)

Ammonia volatilisation can occur when urea fertiliser is applied to soil, urine and dung is deposited on soil and also from the mineralisation of native soil N in organic matter and plant residues (Cameron et al., 2013). Calcareous soils (soils that naturally have a high pH) can lose substantial amounts of NH_3 through volatilisation. Neutral or acid soils can also lose substantial amounts of NH_3 through volatilisation where urea fertiliser is applied (Black et al., 1985). Losses of NH_3 can be substantial when urea fertiliser is applied to soil and can range from 0 to 50% of the N applied (Sommer et al., 2004). After urea fertiliser application, the soil pH is temporarily increased (Black et al., 1995). This is because of the urea hydrolysis process (breakdown of urea granules) where urea ($(NH_2)_2CO$) is converted to ammonium carbonate ($(NH_4)_2CO_3$) which dissociates to produce OH^- ions, NH_4^+, NH_3

and CO_2 (Equation 2.6) which can drive the reaction in equation 2.5 to the right and cause NH_3 loss. Urea hydrolysis occurs in the presence of the ubiquitous soil enzyme urease and occurs around each urea granule and consequently large amounts of N can be lost as NH_3 gas. This process generally occurs within the first few days after application and once the nitrification process becomes significant, the soil pH reduces and so too NH_3 volatilisation (Cameron et al., 2013).

$$(NH_2)_2\,CO + 2H_2O \rightarrow (NH_4)_2\,CO_3 \rightarrow NH_4^+ + NH_3\uparrow + CO_2 + OH^-$$

Equation 2.6 Urea hydrolysis process (Cameron et al., 2013)

Factors affecting NH_3 volatilisation include soil pH, temperature and rainfall/irrigation (Ernst, 1960; Cameron et al., 2013). The effects of soil pH have been explained above but temperature and moisture also affect NH_3 loss with higher NH_3 losses occurring with higher temperatures and lower soil moisture content (Cameron et al., 2013). Under field conditions, the rate of urea hydrolysis and the rate of NH_3 emission follow a diurnal pattern with the highest losses occurring during the highest temperatures (Cameron et al., 2013). Thus on an annual basis, the highest NH_3 emissions would be expected to occur in the warmer months of the year. Black et al. (1985) reported that the highest NH_3 volatilisation rates occurred with high NH_4^+ concentrations at the soil surface along with warm temperatures and elevated soil pH. Rainfall or irrigation can reduce NH_4^+ concentration at the soil surface by washing it below the soil surface, thereby reducing NH_3 losses by up to 80% (Black et al., 1987). Applications of urea are best timed when rainfall is expected to reduce NH_3 volatilisation losses and this is best achieved in Ireland with approximately 7 – 14mm rainfall (Teagasc, 2016a). The addition of urease inhibitors to urea fertiliser are potential mitigation options that can reduce NH_3 emissions by up to 95% (Watson et al., 1994) which are further discussed in section 2.8.1.

Globally, it's estimated that 14% of applied N fertiliser is lost as NH_3 (Bouwman et al., 2002) and agriculture accounts for approximately 50% of all NH_3 volatilised worldwide (Sommer et al., 2004). An average N application rate used for spring barley in Ireland is 150 kg N ha^{-1}. If 14% of this N is lost as ammonia, that represents 21 kg of the applied N that is lost to this one loss pathway. Most of the NH_3 that is volatilised is returned to the earth's surface through wet deposition (dissolved in rainwater) or dry deposition (attached to particulate matter) and this contributes to acidification and eutrophication of natural ecosystems (Cameron et al., 2013). This re-deposition of NH_3 onto land represents an indirect source of N_2O (Cameron et al., 2013) which contributes to GHG emissions.

2.6.5 Nitrate Leaching

Nitrate leaching is the removal of NO_3^- from the soil in drainage water. Nitrate is an anion (i.e. carries a negative charge) and most temperate soils carry a net negative charge and so NO_3^- is repelled and can be easily leached (Di and Cameron, 2000).

Nitrate can be applied to soils directly through N fertilisers or formed during nitrification as explained in the section above. When NO_3^- is transported below the crop rooting system, it can no longer be taken up by the crop and is prone to leaching into groundwater. Nitrate that enters into drinking water can have adverse effects on human health including methaemoglobinaemia in babies (Knobeloch et al., 2000), although this may be just one of a number of other factors that are responsible for this disease (Fewtrell, 2004) and NO_3^- in drinking water can also cause cancer (Ward et al., 2005). The quantity of NO_3^- that is leached from soil depends on the concentration of NO_3^- in soil solution and the quantity of drainage that occurs (Cameron et al., 2013) and leaching is also affected by soil structure

and soil texture (Mulla and Strock, 2008) with higher leaching in coarse-textured soils compared with fine-textured soils (Di and Cameron, 2000).

The amount of NO_3^- leached from the soil depends on the concentration of NO_3^- in the soil solution and the volume of water draining through the soil. Drainage occurs when the soil is at or near field capacity and where water input exceeds evapotranspiration. In Ireland, this period is usually in late autumn, winter and early spring. In arable crops at this time of the year the land is often left fallow where there is no vegetation to take up NO_3^- and so this is the time of the year that is most prone to NO_3^- leaching losses (Di and Cameron, 2000). Research in Ireland has highlighted that spring barley systems can have high nitrate leaching (16 – 95 kg N ha^{-1}) on free draining soils (Hooker et al., 2008).

Leaching occurs through a combination of the three processes convection, diffusion and dispersion (Cameron and Haynes, 1986). Convection is the mass flow of water that contains NO_3^- in it, so the faster the water flows, the more NO_3^- is leached. This is affected by soil texture with higher leaching losses in sandy soils compared to clay soils. This is also affected by soil structure with water flow rates affected by the quantity and size of macropores. Diffusion is the movement of NO_3^- from high concentrations to low concentrations and depends on soil moisture content. Dispersion is the distribution of NO_3^- equally in the soil solution flowing through the soil matrix. Equations for these transport processes are described in Mulla and Strock (2008) and the combined effects of convection, diffusion and dispersion are described by the convective-dispersive equation in Cameron and Haynes (1986).

Nitrogen leaching in arable systems can be higher than in grassland. Williams (1975) observed leaching losses of 51 kg N ha^{-1} yr^{-1} in cultivated cropland compared to only 18 kg N ha^{-1} yr^{-1} in grassland. Cameron et al. (2013) observed leaching losses from arable land

that ranged between 5 – 155 kg N ha^{-1} yr^{-1} depending on N fertiliser applied; soil type and crop rotation system and examples of NO_3^- leaching from cropping systems can be seen in Table 2.2.

Table 2.2 A summary of measured NO_3^- leaching losses from arable crops (adapted from Cameron et al., 2013)

N input (kg N ha^{-1} yr^{-1})	**Soil Type**	**Crop Type**	**NO_3^- leached** (kg N ha^{-1} yr^{-1})	**Location**	**Reference**
0	Silty clay loam	Cereal rotation	8	UK	Goulding, 2000
90	Loamy sand	Spring barley	29	Sweden	Delin and Stenberg, 2014
90	Loamy sand	Spring barley	27	Sweden	Delin and Stenberg, 2014
110	Loamy sand	Spring oats	48	Sweden	Delin and Stenberg, 2014
135	Loamy sand	Spring oats	53	Sweden	Delin and Stenberg, 2014
144	Silty clay loam	Cereal rotation	12	UK	Goulding, 2000
160	Sandy	Spring Barley	71.1	Ireland	Hooker et al., 2008
160	Sandy	Spring Barley	81.9	Ireland	Hooker et al., 2008
160	Loamy sand	Winter Wheat	50	Sweden	Delin and Stenberg, 2014
160	Loamy sand	Winter wheat	80	Sweden	Delin and Stenberg, 2014
169	Clay	Cotton	35	USA	Letey et al., 1977
175	Loamy sand	Winter wheat	4 - 45	UK	Shepherd and Lord, 1996
192	Silty clay loam	Cereal rotation	24	UK	Goulding, 2000
200	Loamy sand	Spring wheat	17 – 87	UK	Shepherd and Lord, 1996
200	Loam	Continuous corn	11 - 107	USA	Bjorneberg et al., 1996
240	Silty clay loam	Cereal rotation	43	UK	Goulding, 2000
288	Silty clay loam	Cereal rotation	58	UK	Goulding, 2000

Mitigation options for NO_3^- leaching from fertilised soils includes the addition of nitrification inhibitors to urea which is discussed in more detail in section 2.8.2

2.7 Nitrogen Fertiliser use in Ireland

Nitrogen fertilisation is a requirement in most arable systems in Ireland in order to achieve optimum crop yields. In malting barley crops particular attention must be paid to the quality of the grain in order to be accepted for malting. These grain quality parameters include moisture content < 18%, screenings (percentage of small grains that pass through a 2.5mm sieve) < 6%, protein content between 8.8 and 10.8% and a germination capacity of 98% (Teagasc, 2016b). Synthetic N fertiliser is a key input in spring malting barley systems with approximately 155 kg N ha^{-1} applied for a 7.5 t ha^{-1} spring barley crop (Teagasc, 2016b) with the expectation that the increased input costs will be offset by the grain yield at harvest. There is continued interest in increasing the yield potential of crop plants in order to provide enough food to feed a growing population. The dominant N fertiliser used in Ireland and Europe is calcium ammonium nitrate (CAN) or CAN based N-P-K compounds. CAN has 27% N, 50% in the ammonium (NH_4^+) form and 50% in the nitrate (NO_3^-) form. Nitrate is the substrate for denitrification which produces N_2O (described in section 1.7.3) and because CAN immediately contributes to the soil NO_3^- pool, it can lead to N_2O losses in favourable conditions. The NH_4^+ can be quickly converted to NO_3^- adding to the soil NO_3^- pool and potentially contributing to further N_2O losses as described in section 1.7.3. An alternative fertiliser that is available in Ireland is urea. However, urea comprises a much smaller proportion of total N sales compared with CAN in Ireland and in 2008 CAN comprised 61% of all N fertilisers used for cereal crops with only 3% urea used and the remainder were compounds (Lalor et al., 2010). However, globally urea is the most used straight N fertiliser. Some studies have shown reduced

yields with urea compared to CAN (Devine an Holmes, 1963; Gately, 1994; Conry, 1997a) which can be explained by NH_3 volatilisation described in section 1.7.4.

Urea contains 46% N and is all in the urea form so it has potential for reducing N_2O emissions compared to CAN as it does not immediately contribute to the soil NO_3^- pool. When urea is applied to soil, N can be lost to the atmosphere as NH_3 gas through the process of NH_3 volatilisation as described in section 1.7.4. Once it is in the ammonium form, it then undergoes the same microbial processes as the ammonium in AN or CAN. Ammonia volatilisation has been shown to be the reason for reduced yields from urea compared to CAN (Chambers and Dampney, 2009). The addition of a urease inhibitor has potential to reduce ammonia volatilisation (Watson et al., 2009; Forrestal et al., 2015) and prevent yield losses compared to using urea on its own. The addition of a nitrification inhibitor has potential to regulate the soil NO_3^- pool and further reduce N_2O emissions.

2.8 Nitrogen stabilisers for reducing N losses

Nitrogen stabilisers (also known as inhibitors) are compounds that can be added to N fertilisers to stabilise the N in the soil and minimise environmental N losses. There are two types of N stabilisers that are commercially available which are urease inhibitors and nitrification inhibitors. “A urease inhibitor is a substance which inhibits hydrolytic action of the urease enzyme on urea” and a nitrification inhibitor is a substance that inhibits the biological oxidation of ammoniacal nitrogen” (Watson et al., 2009). The interaction of N fertiliser formulations, including these N stabilisers, with the N cycle processes, is shown in Figure 2.7. When N stabilisers are added to urea fertiliser, the N remains in the urea form in soil for longer (Watson et al., 2009).

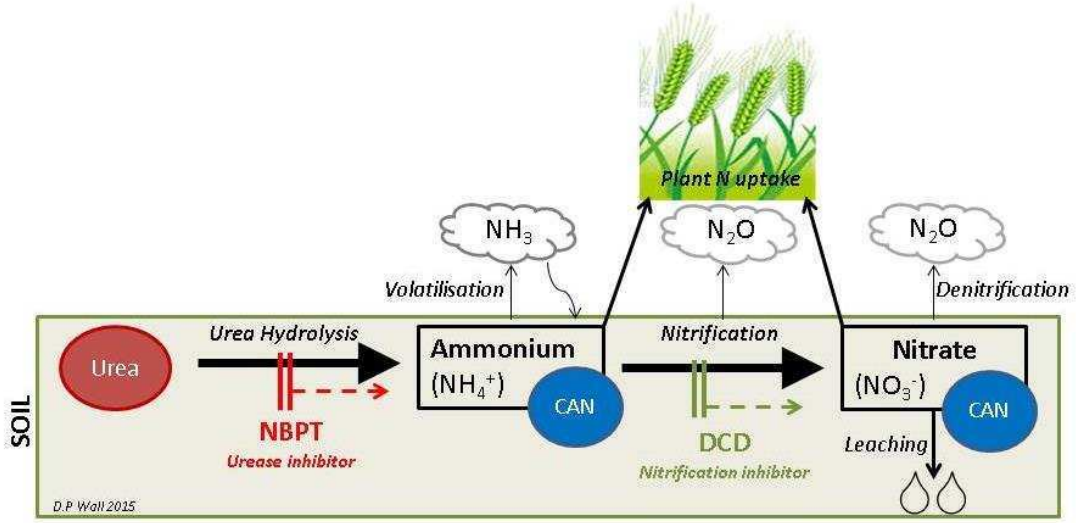

Figure 2.7 Interaction of N fertiliser formulations and the N stabilisers NBPT and DCD with soil N pools

2.8.1 Urease inhibitors

Urease inhibitors are added to urea to slow down the rate of urea hydrolysis to ammonium and therefore reduce the loss of NH_3 through volatilisation (Watson et al., 2009) and increase fNUE. Slowing urea hydrolysis gives urea granules more time to diffuse away from the application site or for rainfall to dilute the urea and NH_4^+ at the soil surface, increasing dispersion into the soil (Watson, 2005). There are many types of urease inhibitors and some of the most effective are the thiophosphorotriamides (Watson et al., 2009). The thiophosphorotriamide compounds are structural analogues of urea and effectively block the active site on the urease enzyme (Watson et al., 2009). The most commonly used thiophosphorotriamide is N-(n-butyl) thiophosphoric triamide (NBPT). This converts to the oxygen analogue N-(n-butyl) phosphoric triamide which is what the inhibitory activity is associated with and this conversion is rapid, occurring within in minutes or hours (Byrnes and Freney, 1995). Many studies have shown that the addition of

NBPT to urea can reduce NH_3 volatilisation losses (Trenkel, 1997; Watson, 2005; Forrestal et al., 2015) and some studies have shown the addition of NBPT to urea to increase yields (Grant and Bailey, 1999). Harty et al. (2016) observed urea + NBPT to significantly reduce N_2O emissions relative to CAN on Irish grasslands. The addition of NBPT to urea has potential to be cost effective and have environmental benefits compared to using CAN (Watson, 2005).

2.8.2 Nitrification inhibitors

Nitrification inhibitors delay the oxidation of NH_4^+ by blocking the *AmoA* gene in nitrifying microbes by blocking the site where ammonium is converted to hydroxylamine (Figure 2.8) (Watson et al., 2009). This ultimately slows down the conversion of NH_4^+ to NO_3^- and maintains N in the soil in the NH_4^+ form for longer and therefore reduces NO_3^- leaching and the production of N_2O by nitrification and denitrification, potentially increasing fNUE.

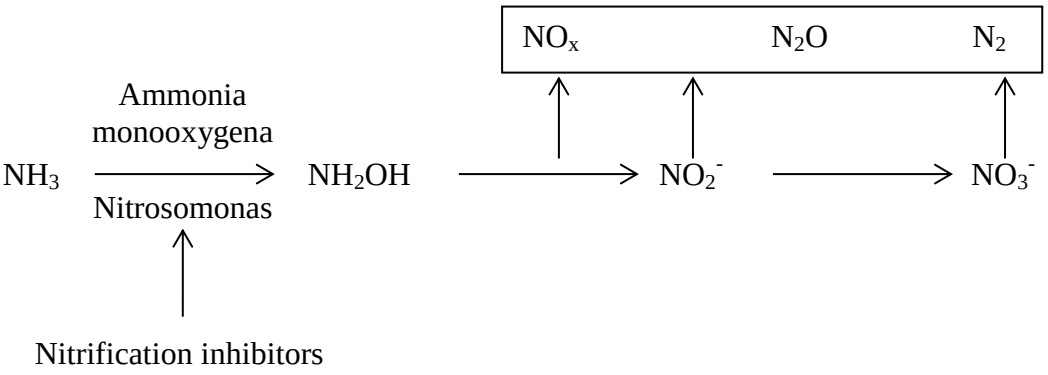

Figure 2.8 Nitrification inhibitors blocking the site where NH_4^+ is converted to hydroxylamine (Watson et al., 2009)

There are a number of different nitrification inhibitors which have been studied including 3, 4 – Dimethylpyrazole phosphate (DMPP) (Zerulla et al., 2001), Dicyandiamide (DCD) (Amberger, 1989), extract of neem (Sahrawat, 1975), nitrapyrin (Belsar and Schmidt, 1981) but the most commonly used nitrification inhibitor is DCD (Watson et al., 2009).

As nitrification inhibitors slow down the rate of nitrification and maintain the N in the soil as NH_4^+ N for longer, some studies have shown a significant increase in NH_3 losses (Zaman et al., 2009 – increase in NH_3 emissions in a grazed pasture system when applied to urine). A meta-analysis by Kim et al. (2012) studied 46 datasets from 21 studies from 1970 and 2010 and concluded that using nitrification inhibitors increased NH_3 emissions but the magnitude of the increase was dependent on pH and cation exchange capacity (CEC).

Several studies have shown that the addition of DCD to urea can reduce N_2O emissions (McTaggart et al 1997; Weiske et al., 2001; Harty et al., 2016a; Roche et al., 2016) but some studies have shown reduced yields using DCD (Harty et al., 2016b).

Switching from straight CAN to urea N formulations amended with N stabilisers has the potential to reduce gaseous losses of N and a summary of gaseous N decreases from N stabilisers is shown in Table 2.3. Switching from CAN to urea also has the potential to increase yields and maintain an optimum grain N content. This is a win-win scenario for achieving GHG reduction targets and achieving production targets set out in FW 2025.

Table 2.3 A summary of NH_3 and N_2O reductions using urea stabilised with NBPT and DCD

Reference	Country	Soil Texture	N Fertiliser	N stabiliser	Crop	NH_3 reduction	N_2O reduction
McTaggart & Smith 1997	Scotland	Clay loam	Urea	Urea + DCD	Grassland		57%
McTaggart & Smith 1997	Scotland	Loam	Urea	Urea + DCD	Barley		40%
Rawluk et al., 2001	Canada	Clay loam	Urea	Urea + NBPT		Up to 85%	
Rawluk et al., 2001	Canada	Sandy clay loam	Urea	Urea + NBPT		Up to 37%	
Sanz-cobena., 2008	Spain	Loam	Urea	NBPT	Sunflower	58%	
Abalos et al., 2012	Spain	Clay loam	Urea	NBPT	Barley	58%	86%
Sanz-cobena et al., 2012	Spain	Sandy clay loam	Urea	Urea + NBPT	Maize		54%
Sanz-Cobena, 2012	Spain	Sandy clay loam	Urea	DCD	Maize		24%
Bell et al., 2015	England	Sandy clay loam	AN	Urea + DCD	Spring Barley		68%
Bell et al., 2015	England	Clay loam	AN	Urea + DCD	Winter wheat		14%
Bell et al., 2015	Scotland	Loamy sand over sandy loam	AN	Urea + DCD	Winter wheat		34%
Forrestal et al., 2015	Ireland		Urea	Urea + NBPT	Grassland	73%	
Roche et al., 2016	Ireland	Loam	CAN	Urea + NBPT	Spring barley		43%
Roche et al., 2016	Ireland	Loam	CAN	Urea + DCD	Spring barley		63%
Harty et al., 2016	Ireland	Sandy loam	CAN	Urea + DCD	Grassland		64%
Harty et al., 2016	Ireland	Sandy loam	CAN	Urea + DCD	Grassland		66%
Harty et al., 2016	Ireland	Sandy loam	CAN	Urea + DCD	Grassland		47%
Harty et al., 2016	Ireland	Sandy loam	CAN	Urea + DCD	Grassland		51%
Harty et al., 2016	Northern Ireland	Clay loam	CAN	Urea + DCD	Grassland		94%
Harty et al., 2016	Northern Ireland	Clay loam	CAN	Urea + DCD	Grassland		84%

2.9 Plant N Uptake

Plants can take up many forms of N including N_2, NH_3, nitrogen oxides (NO_x), mineral N (NO_3^- and NH_4^+) and organic N including amino acids (von Wiren et al., 1997). The uptake of N_2 is only relevant for leguminous plants that can form a symbiosis with N-fixing bacteria (von Wiren et al., 1997). In agricultural soils, it is mineral N that is primarily taken up by plants but this depends on soil conditions and plant species. In most agricultural soils, N is taken by the roots as NO_3^- because NO_3^- generally occurs in higher concentrations and is free to move within the root soil solution due to fact that NO_3^- is an anion and soils tend to have an overall net negative charge (Miller and Cramer, 2005).

The uptake of NH_4^+ occurs in low pH soils and reducing soil conditions whereas NO_3^- uptake is more dominant in higher pH and more aerobic soils (Maathuis, 2009). Soil N availability is affected by precipitation, temperature, wind, soil type and soil pH (Maathuis, 2009). The mineralisation of organic N is generally not sufficient for common agricultural crops to produce optimum yields and so, N fertiliser is required. Nitrogen fertilisation strategies are optimised to produce high yields and minimise N losses. Fertiliser N for arable crops should be applied in a small application rate of around 30 kg N ha^{-1} at sowing and the remainder during tillering (Baethgen et al., 1995) which is the fertilisation strategy used in Ireland. This is because the crop only needs a little N for crop emergence but after mid-tillering there is a rapid phase of N uptake and this is when the higher quantity of N is required (Teagasc, 2016b).

Nitrogen uptake occurs at different levels during different growth stages (Figure 2.9). A spring barley crop takes up approximately 0.9 kg N ha^{-1} d^{-1} from sowing until Zadoks growth stage (GS) 32 (Zadoks et al., 1974), approximately 1.2 kg N ha^{-1} d^{-1} from GS 32 –

GS 59 and approximately 0.5 kg N ha^{-1} d^{-1} from GS 59 – GS 87 with the total uptake at GS 87 approximately 151 kg N ha^{-1} (Teagasc, 2016b).

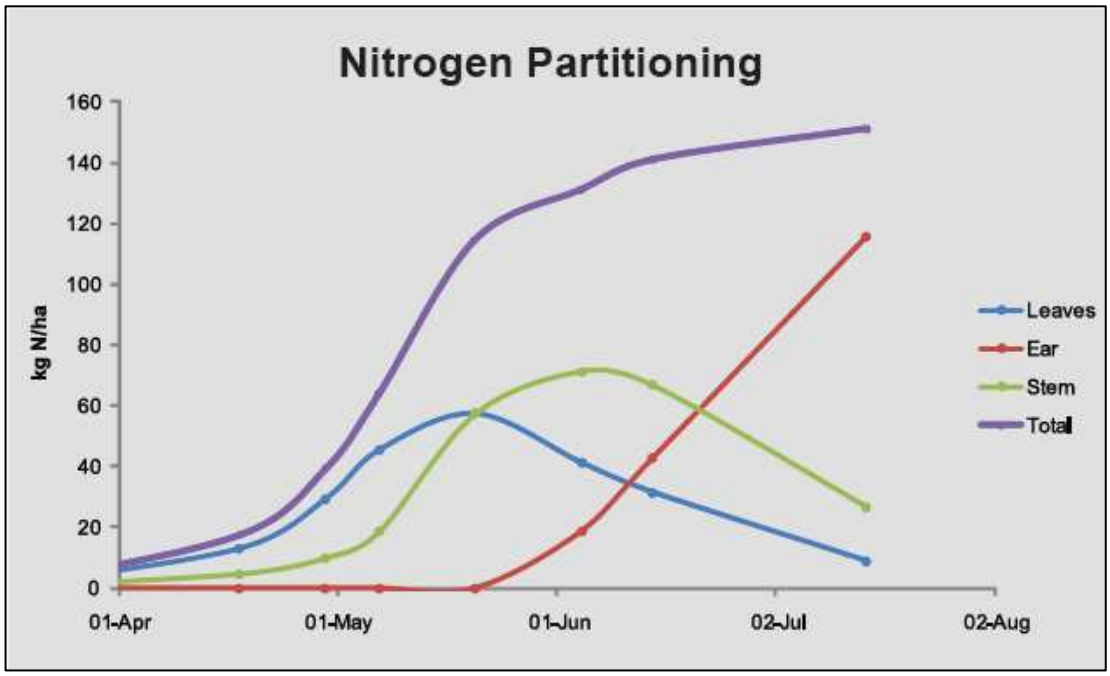

Figure 2.9 Nitrogen partitioning in spring barley (Teagasc, 2016b)

2.10 N recommendation system for spring barley in Ireland

Spring barley is the most extensively grown arable crop in Ireland accounting for approximately 46% of the arable farming area (CSO, 2016). Agriculture in Ireland relies heavily on synthetic N fertiliser inputs. The N recommendation system used for spring barley in Ireland is based primarily on the WFD and the ND (described in section 2.4) and sets out maximum allowable N and P inputs. Maximum allowable limits are based on an N index system depending on the cropping history of the land (Table 2.4). The maximum allowable N input for spring barley for index 1 is 135 kg N ha^{-1}, index 2 is 100 kg N ha^{-1}, index 3 is 75 kg N ha^{-1} and index 4 is 40 kg N ha^{-1}. Where there is proof of higher yields above 6.5 t ha^{-1} an additional 20 kg N ha^{-1} per additional tonne of grain is allowed. Where malting barley is grown under contract an additional 20 kg N ha^{-1} may be applied on the

basis of agronomic advice that additional N is required to address proven low protein content in the grain.

Table 2.4 Nitrogen Index system used in Ireland for tillage crops

Tillage crops that follow permanent pasture			
Nitrogen Index			
Index 1	**Index 2**	**Index 3**	**Index 4**
The 5th tillage crop following permanent pasture. For subsequent tillage crops use the continuous tillage table	The 3rd or 4th tillage crop following permanent pasture. If original permanent pasture was cut only, use index 1	The 1st or 2nd tillage crop following permanent pasture (see also index 4). If original permanent pasture was cut, use index 2	The 1st or 2nd tillage crop following very good permanent pasture which was grazed only
Continuous tillage: - crops that follow short leys (1 – 4 years) or tillage crops			
Previous crop			
Index 1	**Index 2**	**Index 3**	**Index 4**
Cereals Maize	Sugar beet Fodder beet Potatoes Mangels Kale Oil seed rape, peas, Beans		
	Leys (1 – 4 years) grazed or cut and grazed		
	Swedes removed	Swedes grazed in situ	
Vegetables receiving less than 200 kg/ha nitrogen	Vegetables receiving more than 200 kg/ha nitrogen		

The aims to reduce N losses under the WFD and ND for protecting water quality also result in reductions in greenhouse gas emissions and help member states achieve reduction targets of 20% by 2020 set out in the Kyoto Protocol. Agriculture practices may contribute to GHGs (including indirect losses through ammonia volatilisation and nitrate leaching) in the atmosphere which is the main driver for climate change and global warming.

2.10.1 Spring barley production in Ireland

Barley is one of the most important crops globally with 55 million hectares produced worldwide with a global production of 132 million tons (Akar et al., 2004). Approximately 62% of global barley production is in Europe and Ireland achieves the third highest yields, per hectare, of barley in the EU (FAO, 2016b).

Spring barley is the most extensively grown cereal crop in Ireland accounting for approximately 46% of the arable farming area (CSO, 2016) and is grown for animal feed and malting industries. Spring barley is suited to many Irish soils and can perform consistently well in continuous production in farms that have limited opportunities for break-crops (Teagasc, 2016b) but yields are variable typically ranging from 6.1 – 7.7 t ha^{-1} between 2008 – 2015 (CSO, 2013, 2015, 2016). Teagasc have developed a comprehensive guide for growing spring barley in Ireland which details the required crop management for optimising yields (Teagasc, 2016b).

In recent years, there has been concern amongst growers that the maximum allowable N rates for spring barley which are set out in the ND are not sufficient to consistently produce high yields and are compromising grower's ability to produce malting barley with acceptable protein levels (Hackett, 2014). There are a number of grain quality criteria that must be reached before spring barley will be accepted for malting purposes and these are discussed in the Teagasc Spring Barley Guide (Teagasc, 2016b).

If the grain quality parameters, including an optimum protein range are not met, then the marketability of this grain for malting purposes will be diminished representing significant financial losses for these farmers. If this results in a national shortfall in malting barley supply, it would inevitably lead to malting companies sourcing their malt elsewhere leading to major financial losses to the Irish tillage sector.

The preferred protein content of the grain is between 8.8 and 10.8% (Teagasc, 2016b) and for distilling, the grain protein content should be between 8.5 and 9.3% (Teagasc, 2016b). High protein levels (greater than 11%) lead to lower starch content, which result in less alcohol and cloudy beer whereas low protein levels (lower than 9.5%) limit yeast activity due to lack of N (Pettersson and Eckersten, 2007). Farmers grow malting barley as it receives a higher price than feed barley but these grain quality requirements must be adhered to in order for grain to be accepted for malting purposes.

The tillage sector development plan has set out projections of increases in the tillage sector by 2020 (Teagasc, 2012). An increase of 115,000 t of barley for malting purposes is projected. In order to achieve this target, further research is needed to improve crop yields and achieve grain quality standards that are required by maltsters. Grain protein content is an indicator of the adequacy of fertiliser N application in commercial fields, with low protein indicating insufficient fertiliser N application (Sylvester-Bradley, 2009). However, Hackett (2014) showed that this is very variable between sites and years and concluded that the total amount of N applied is the most important factor influencing grain protein content.

Some of the N taken up by the barley crop is translocated to the grain where it is metabolised into grain protein. Therefore it is vital to ensure that adequate N fertiliser to produce the required grain protein content is applied. Given the reported low protein levels in spring malting barley in Ireland in recent years (2007 - 2011), the levels of N fertiliser recommended and/or applied may not have been adequate to achieve target grain yield and quality on farms.

When fertiliser N is applied to soil it can be lost through ammonia volatilisation (described in section 1.7.4), nitrification (described in section 1.7.2) and also denitrification

(described in section 1.7.3). These N losses represent an economic loss to farmers and will result in lower N uptake potential by the crop. Plant N uptake is approximately 50% of the N applied (Watson et al., 2009). Therefore, it is important to re-evaluate the current N recommendations to ascertain if higher N fertiliser application rates or different N fertiliser types are required for spring barley crops, and what effects, if any, these would have on N losses from these systems.

A balance is needed between agronomic factors that produce high yields and those that produce good quality grain for maltsters (Conry, 1997). It has been shown in many studies that grain yields and quality can be affected by site and season differences (Conry 1997; Hackett 2014). Changing fertiliser type may have different effects on different sites and in different climates.

Using N stabilisers has the potential to increase grain yield and N uptake in the crop as it maintains the N in the soil for longer. Nitrogen stabilisers have been shown to reduce N losses of NH_3, N_2O and NO_3^- leaching as described in sections 2.6.2, 2.6.3, 2.6.4, 2.6.5 but the impact of these N stabilisers on grain yield is an important factor to consider. Abalos et al. (2014) reported that using N stabilisers could increase grain yield by 7.5% and fNUE by 12.9%. A recent study on grassland in Ireland showed no difference in yield between CAN and urea + NBPT but showed yield reductions with urea + DCD compared to CAN (Harty et al., 2016b). However Bell et al. (2015) showed no difference in yields between CAN and urea + DCD in spring barley.

There is potential for using N stabilisers in spring barley to increase yields and N uptake as well as reduce environmental losses of N representing a win-win scenario.

2.11 Summary of Literature Review

This literature review has highlighted the obligations that Ireland has to reduce GHG emissions and that, in Ireland, agriculture is the largest contributor to GHG emissions, accounting for approximately one third of total GHG inputs to the atmosphere. In arable systems, the main contribution to GHGs is the application of N fertilisers producing N_2O emissions through nitrification and denitrification. The typical N fertiliser that is used in Ireland is CAN which contributes to N_2O emissions and NO_3^- leaching as it immediately adds to the soil NO_3^- pool. Switching to a urea based fertiliser has potential to reduce these losses as it does not immediately contribute to the soil NO_3^- pool and the N must go through transformations in the soil before being present in forms that are most susceptible to loss. When urea is applied to soil it undergoes urea hydrolysis to convert the N to NH_4^+ which may be subject to subsequent volatilization loss as NH_3. Volatilized NH_3 is considered an indirect GHG as it can be re-deposited on the surface and can then undergo nitrification and denitrification and can contribute to N_2O emissions. The addition of N stabilisers to urea can reduce these N losses as the transformation processes are slowed down thereby releasing smaller amounts of NH_4^+ and NO_3^- for plant uptake which would result in less N losses.

Switching N fertiliser source from CAN to urea could potentially reduce environmental N losses of NO_3^-, N_2O and NH_3 and has potential for maintaining or even increasing crop yields and quality. This represents a win-win scenario for both environmental loss reduction targets and production targets.

2.12 Objectives and Hypothesis of this Thesis

The objectives and hypotheses of this thesis are:

- To quantify the effect of CAN and urea on N_2O emissions in spring barley and to assess the mitigation effect of the urease inhibitor NBPT and the nitrification inhibitor DCD at reducing N_2O emissions
    - *Hypothesis : The addition of N stabilisers to urea will reduce N_2O emissions compared to CAN*

- To quantify the effect of CAN and urea on NO_3^- leaching from spring barley and to assess the mitigation effect of urea stabilised with NBPT + DCD at reducing NO_3^--N leaching compared to CAN
    - *Hypothesis: The addition of N stabilisers to urea will reduce NO_3^- leaching compared to CAN, and increasing N fertiliser rate will increase NO_3^--N leaching*

- To assess the effect of CAN and urea on NH_3 emissions in spring barley in Ireland and to assess the effect of the urease inhibitor NBPT at reducing NH_3 emissions compared to urea.
    - *Hypothesis: The addition of the urease inhibitor NBPT to urea will reduce NH_3 emissions compared to urea and will be similar to CAN*

- To quantify the effect of CAN and urea and urea with N stabilisers on spring barley grain yield and N uptake.
    - *Hypothesis : Switching N fertiliser formulation from CAN to urea with N stabilisers will not negatively impact grain yield, crop N uptake or grain protein content*

2.13 Layout of Thesis

A flowchart showing the structure of the thesis is shown in Figure 2.10. This shows how the thesis flows from one chapter to the next and describes the contents of each individual chapter ending with an overall discussion and conclusions chapter.

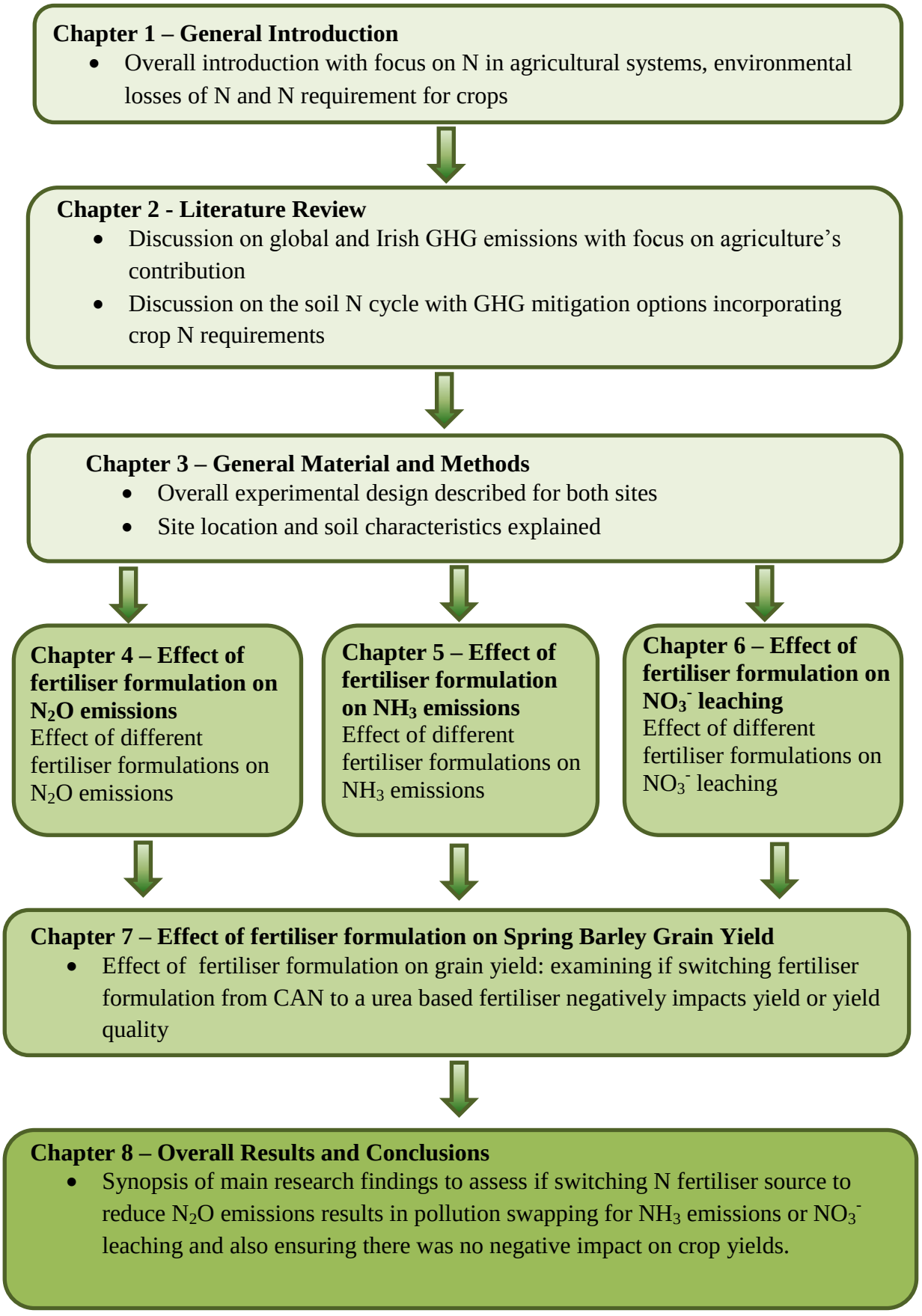

Figure 2.10 Flowchart of Thesis

Chapter 3 - General Materials and Methods

3.1 Introduction

This PhD project comprised four different experiments which will be described in the subsequent chapters, focusing on the fate and transport of different N fertiliser formulations in spring barley in Ireland:

- A two year plot based field experiment measuring N_2O emissions from different N fertiliser formulations and generating N_2O emission factors (Chapter 4)
- A two year plot based experiment measuring NO_3^- leaching from different N fertiliser formulations (Chapter 5)
- A three week experiment measuring ammonia emissions from different N fertiliser formulations (Chapter 6)
- A three year plot based experiment measuring spring barley grain yield and N uptake from different N fertiliser formulations (Chapter 7)

These experiments were established on two experimental field sites located in Co. Wexford in Ireland and the aim of this chapter is to describe the sites location and soil characteristics as well as the experimental design.

3.2 Site locations and soil characteristics

The two experimental field sites were located in Marshalstown, Co. Wexford (MT) and Johnstown Castle, Co. Wexford (JC) which is located in the south east of Ireland (Figure 3.1). The soil characteristics of both sites can be seen in Table 3.1 and are based on the top 10cm of soil, the standard agronomic soil sampling depth used in Ireland.

3.2.1 Johnstown Castle field site

Johnstown Castle is a short-term arable site which has been in maize for three years prior to this experiment and then cropped with spring barley for three years for this experiment. Before this, it was a permanent grassland site. While in grassland and cropped with maize, this site received annual applications of organic manure with the last application in winter 2012, six months before the current experiment began. Nitrate leaching, NH_3 emissions and grain yield and N uptake were measured at JC and the overall experimental design can be seen in Figure 3.2.

3.2.2 Marshalstown field site

Marshalstown is a long-term arable site that has been in arable production for over 20 years and cropped with continuous spring barley since 2007. This site is located within the Castledockrell agricultural catchment. The agricultural Catchments Programme (ACP) was set up with the aim of evaluating the environmental and economic effects of the Nitrates Action Plan measures implemented under the Nitrates Directive. There are six agricultural catchments located across Ireland and the Castledockrell catchment is one of these which includes both grassland and arable on free draining soils. Nitrate leaching, NH_3 emissions, N_2O emissions and grain yield and N uptake were measured at MT and the overall experimental design can be seen in Figure 3.3.

3.3 Experimental Design

A randomised block design was used with five replicates of each treatment for grain yield, N uptake and N_2O emissions (Figure 3.2 and Figure 3.3). The blocks are shown in different colours for the experimental design at each site and were laid out in this way to fit in the allotted area. For each plot there were two subplots. The larger plot measured 12m x 2.5m and was for agronomy measurements including grain yield and N uptake. The smaller plot measured 6m x 2.5m and was where N_2O emissions were measured and soil sampling took place. N_2O chambers were only installed at the MT site as this site is typical of spring barley land in Ireland. Lysimeters were installed at both sites, 24 lysimeters at JC and 18 in total in at MT (16 were installed in 2013 and a further 2 were installed in 2014 which can be identified in red in Figure 3) and there were four replicates of each treatment in this experiment. Ammonia emissions were measured at both sites in 2014 and at MT only in 2015 using passive shuttles on masts 0.7m high and 10m diameter and there were 2 replicates of each treatment for this experiment. A list of the treatments studied and more detailed descriptions are in the subsequent chapters.

Figure 3.1 Experimental Field site locations *1 is Johnstown Castle (JC) and 2 is Marshalstown (MT)

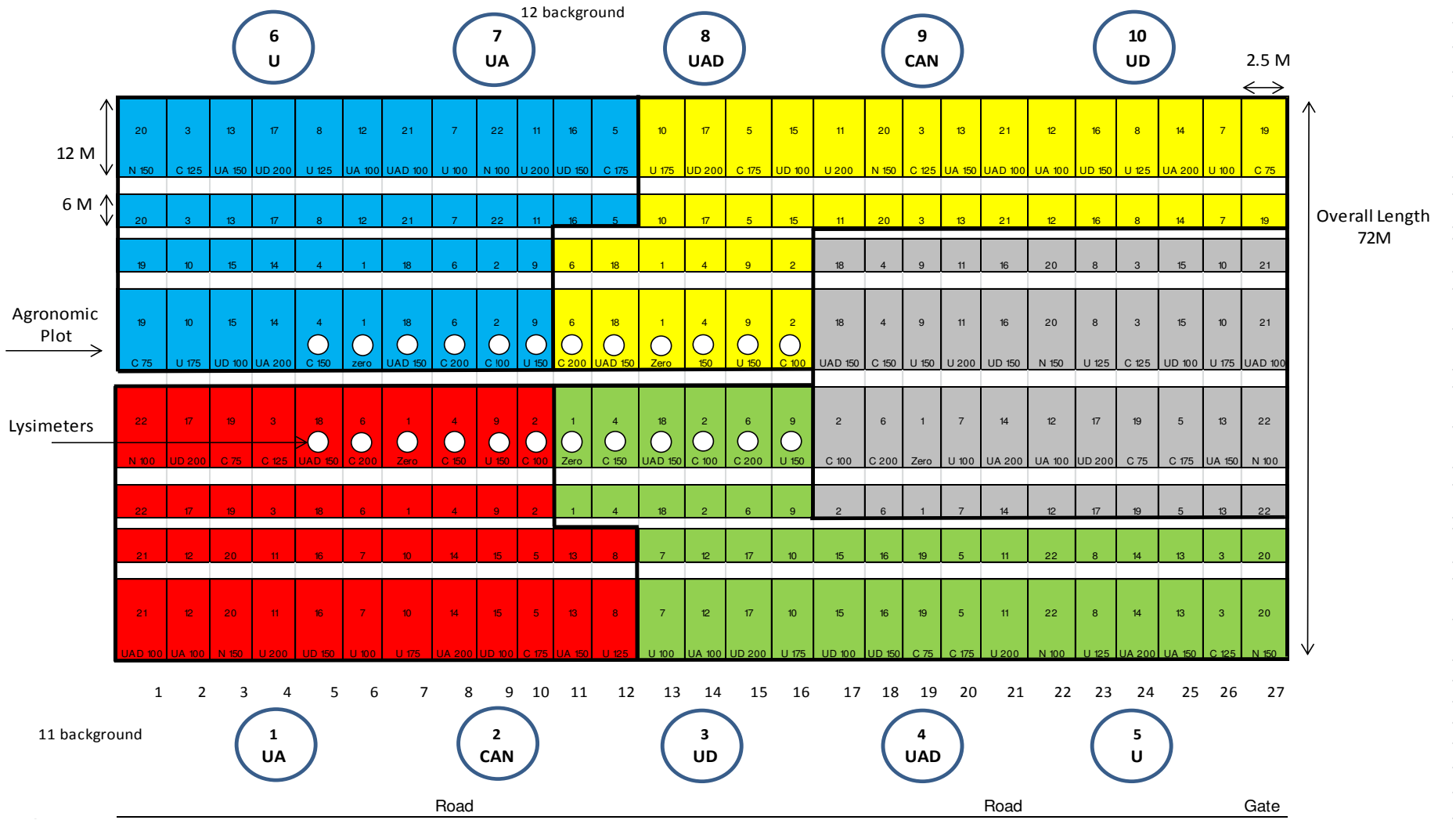

Figure 3.2 Overall experimental design for Johnstown Castle showing treatment blocking structure (five replicates in total) with agronomic plots for measuring grain yield and N uptake, plots with lysimeters for measuring NO_3^- leaching and plots with passive shuttles for measuring NH_3 concentrations

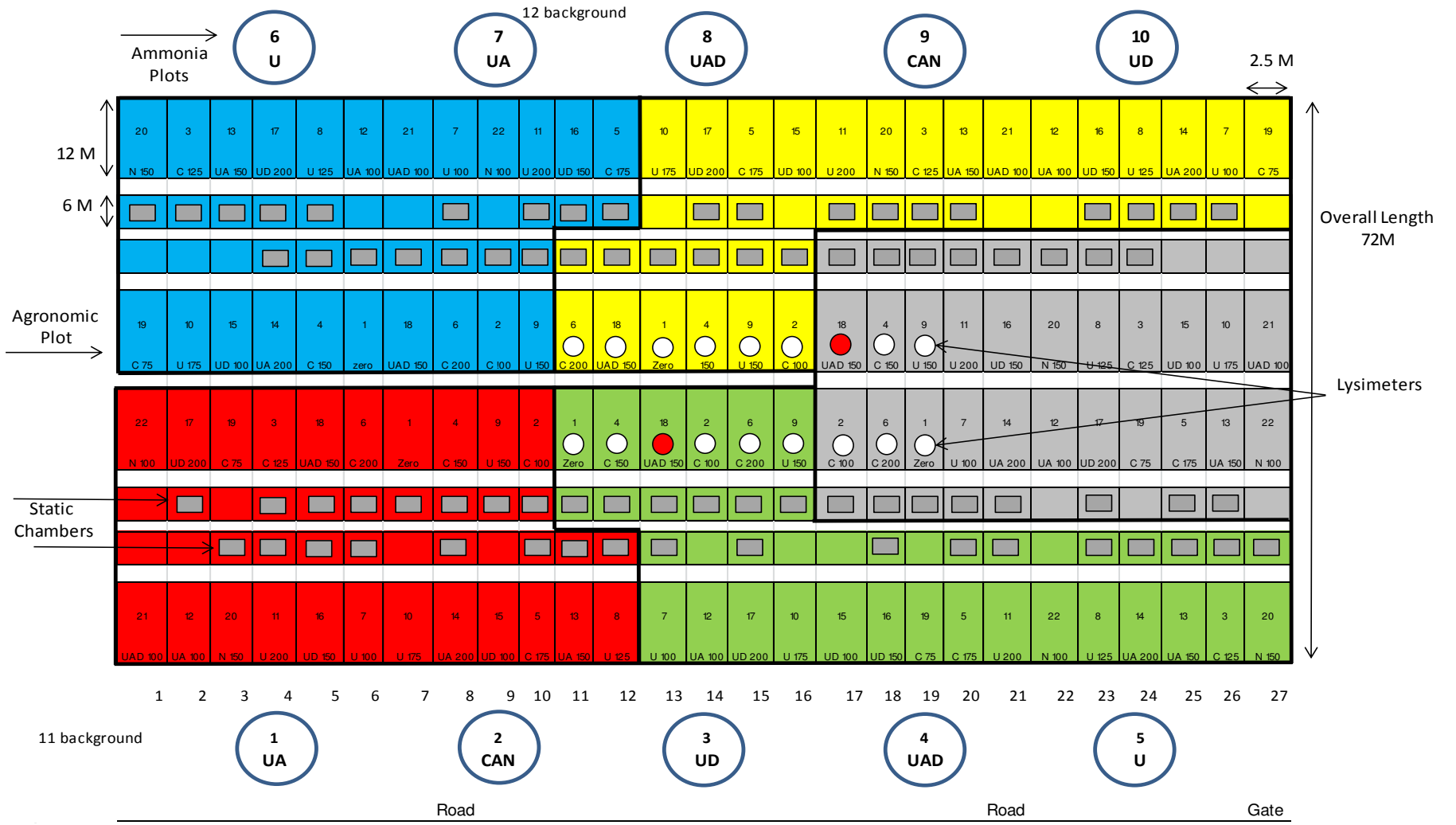

Figure 3.3 Overall experimental design for Marshalstown showing treatment blocking structure (five replicates in total) with agronomic plots for measuring grain yield and N uptake, plots with static chambers for measuring N_2O emissions, plots with lysimeters for measuring NO_3^- leaching and plots with passive shuttles for measuring NH_3 concentrations

Table 3.1 Site locations and soil physical and chemical properties for both experimental field sites (0-10 cm)

	Marshalstown (MT)	**Johnstown (JC)**
GPS Co-ordinates	52° 33' 37.3" N 6° 36' 09.0" W	52° 18' 04.6" N 6° 30' 26.9" W
Drainage Class	Free- draining	Moderately draining
Soil Texture	Loam	Sandy-loam
Sand %	31.8	57.7
Silt %	41.4	30
Stone volume (v/v)	28	4
Soil pH	6.76	6.46
CEC (meq/100g)	21.1	15.95
Soil Ca (mg/l soil)	1574	1176
Soil K (mg/l soil)	260	285
Soil Mg (mg/l soil)	160	72
Soil P (mg/l soil)	36.3	37.9
Soil S (mg/l soil)	4.66	7.47
Soil LOI %	8.99	6.42
Total C %	2.88	2.37
Total N %	0.281	0.224
C : N ratio	10	11

3.4 Crop Husbandry

The spring barley (Hordeum vulgare L.) cultivar that was used on both sites over the full study was *C.V.*'Sebastian' which is a malting variety. The sites were ploughed to approximately 20cm – 30cm depth in February/ March each year using a mouldboard plough. Crop sowing dates for each site and year can be seen in Table 3.2 and N fertiliser application dates can be seen in Table 3.3. Each year basal P, K and S were applied to the soil according to the Teagasc green book of nutrient advice (Coulter and Lalor, 2008) to prevent nutrient deficiencies from occurring. A robust pesticide/ insecticide/ fungicide programme was applied to the crop to control weeds, pests and diseases as per standard agronomic practices for spring barley crops in Ireland (Teagasc, 2015).

Table 3.2 Crop sowing dates for each site and year

Site	Year	Sowing Date
Johnstown Castle	2013	09/04/2013
Johnstown Castle	2014	15/04/2014
Marshalstown	2013	08/04/2013
Marshalstown	2014	14/04/2014
Marshalstown	2015	27/03/2015

Table 3.3 Nitrogen fertiliser application dates for 1st and 2nd split applications for each site and year

	1st split (30 kg N ha^{-1})	2nd split (remainder fertiliser (kg N ha^{-1}))
	Date Applied	Date applied
2013		
MT	15/04/2013	13/05/2013
JC	15/04/2013	13/05/2013
2014		
MT	23/04/2014	13/05/2014
JC	23/04/2014	13/05/2014
2015		
MT	01/04/2015	20/04/2015

Chapter 4 - Impact of fertiliser nitrogen formulation and N stabilisers on nitrous oxide emissions in spring barley

Chapter 4 has been published with Agriculture, Ecosystems and Environment Journal in 2016 and the full journal article is shown in appendix B.

Agriculture, Ecosystems and Environment 233 (2016) 229–237

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley

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ARTICLE INFO

Article history:
Received 5 May 2016
Received in revised form 24 August 2016
Accepted 27 August 2016
Available online xxx

Keywords:
Urea
Emission factor
Arable soil
DCD
Inhibitors
NBPT

ABSTRACT

The application of nitrogen (N) fertilisers to agricultural soils is a major source of nitrous oxide (N_2O) emissions. The Intergovernmental Panel on Climate Change (IPCC) has set a default emission factor of 1% (EF_1) for N fertiliser applied to managed agricultural soils. This value does not differentiate between different N fertiliser formulations or rates of N application. The objective of this field study under spring barley was to determine N_2O EF's for different N fertiliser formulations including urea and urea stabilised with the nitrification inhibitor dicyandiamide (DCD) and/or the urease inhibitor *N*-(*n*-butyl) thiophosphoric triamide (NBPT) and to evaluate their N_2O loss abatement potential relative to calcium ammonium nitrate (CAN). The highest EF_1 measured was 0.49% for CAN which was less than half the IPCC default value of 1%. While the urease inhibitor did not reduce emissions relative to CAN; the nitrification inhibitor significantly reduced emissions compared to CAN with EF_1 as low as 0.00% for a typical spring barley site. There was no significant impact of CAN or urea application rate on EF_1 but there was a significant negative relationship observed for urea in 2013. The study highlights the importance of generating higher Tier emission factors in terms of fertiliser type for use in national inventories.

4.1 Summary

The application of nitrogen (N) fertilisers to agricultural soils is a major source of N_2O emissions. The Intergovernmental Panel on Climate Change (IPCC) has set a default emission factor of 1% (EF_1) for N fertiliser applied to managed agricultural soils. This value does not differentiate between different N fertiliser formulations or rates of N application. The objective of this field study under spring barley was to determine N_2O EF's for different N fertiliser formulations including urea and urea stabilised with the urease inhibitor *N*-(*n*-butyl) thiophosphoric triamide (NBPT) and/or the nitrification inhibitor dicyandiamide (DCD) and to evaluate their N_2O loss abatement potential relative to calcium ammonium nitrate (CAN). The highest EF_1 measured was 0.49% for CAN which was less than half the IPCC default value of 1%. While the urease inhibitor did not reduce emissions relative to CAN; the nitrification inhibitor significantly reduced emissions compared to CAN with EF_1 as low as 0.00% for a typical spring barley site. There was no significant impact of CAN or urea application rate on EF_1 but there was a significant negative relationship observed for urea in 2013. This study highlights the importance of generating higher Tier emission factors in terms of fertiliser type for use in national inventories.

4.2 Introduction

Concentrations of atmospheric GHGs have increased since the beginning of the industrial era, due to anthropogenic activities (U.S. EPA, 2015). Between 1990 and 2005, global non-carbon dioxide (CO_2) GHG emissions grew by 10% to approximately 10,800 megatons CO_2 equivalent (Mt CO_2 eq) and are expected to increase by 43% by 2030 (U.S. EPA, 2012). Globally, the agriculture sector accounts for the largest proportion of non-CO_2 GHG emissions, accounting for 54% in 2005 (U.S. EPA, 2012). Nitrous oxide comprises approximately 32% of agricultural emissions (U.S. EPA, 2012) and is a potent GHG, with a global warming potential 265 times that of CO_2 over a 100 year time frame (Myhre et al., 2013). The atmospheric concentration of N_2O has increased at an average rate of 0.75 ppb yr^{-1}, rising 20% since 1750 to 324 ppb (IPCC, 2014). Emissions associated with nitrogen (N) application to agricultural soils comprise 60% of global N_2O emissions and are projected to increase from 6.1 to over 7 Tg N_2O-N yr^{-1} by 2030, due to increased global population and food demand (Reay et al., 2012). The use of mineral fertilisers has been one of the principal drivers of this increase in emissions (Davidson, 2009). Excess N application has resulted in enhanced reactive N losses to the environment (Bell et al., 2015). Furthermore N_2O is the single most important ozone-depleting gas and is expected to remain so throughout the 21st century (Ravishankara et al., 2009).

In order to generate total N_2O emissions for inputting into national inventories, the quantity of a given activity (e.g. tonnes of fertiliser applied) is multiplied by an emission factor (EF). This emission factor is defined as the percentage of N_2O emitted as a proportion of the N applied. The IPCC default EF for direct N_2O emissions, associated with the application of mineral or organic fertiliser to managed soils, (termed EF_1) is 1% of the N applied (IPCC, 2006). This value is a crude estimate as it does not account for crop and

soil type, climatic conditions or management practices, all of which affect N_2O emissions (Dobbie et al., 1999; Dobbie and Smith, 2003a, 2003b; Lesschen et al., 2011). Country and cropping system specific data would allow temperate regions to use the Tier 2 emission inventory methodology, where these more detailed and accurate emission factors that are specific for soil and crop type are required (IPCC, 2006). Subsequently, these data could support the development of new N fertiliser recommendations in Ireland; therefore promoting continued reductions of GHG emissions in line with the 2030 targets to reduce GHG emissions by 40% (EC, 2014).

In Ireland the agricultural sector contributes 32% of national GHG emissions (Duffy et al., 2015). Nitrogen application to agricultural soils is one of the key categories, accounting for 22% of total emissions from agriculture and this is projected to increase by 12% by 2020 (EPA, 2013). The focus of this study is on arable land, specifically examining the N_2O emissions resulting from the addition of N fertiliser to spring cereal crops, which is one of the largest contributors to GHGs from this land use type. Altering fertiliser formulation and/or rate as well as the incorporation of inhibitors may be a key abatement strategy for reducing N_2O emissions from agriculture (Harty et al., 2016a).

Calcium ammonium nitrate (CAN) is the dominant N fertiliser used by arable farmers in Ireland. CAN contains 27% N, of which 50% is in the nitrate-N form and immediately contributes to the soil nitrate pool. Nitrate is then available for N_2O loss through the denitrification processes. Nitrification may also be an important source of N_2O from the application of urea or ammonium based fertilisers (Bremner and Blackmer, 1978). Substituting CAN with urea as an alternative N fertiliser formulation has the potential to reduce direct N_2O emissions, associated with denitrification, because urea or ammonium N forms are not immediately available for denitrification after application. However, there

is potential for nitrifier denitrification to be a source of N_2O (Kool et al., 2011) coupled with the potential for urea to favour N loss as ammonia during urea hydrolysis. The addition of a urease inhibitor has potential to reduce ammonia volatilisation which not only contributes to air pollution but which can also contribute to indirect N_2O emissions (Watson et al., 2009; Forrestal et al., 2015). The addition of a nitrification inhibitor has potential to regulate the soil nitrate pool and further reduce direct N_2O emissions by both nitrification and denitrification (Dobbie and Smith, 2003a). The rate of N fertiliser application is also important as generally the higher the N fertiliser rate, the higher the N_2O emissions (Hinton et al., 2015). Using the IPCC default EF_1 assumes a linear relationship between N_2O emissions and N fertiliser rate which Hinton et al. (2015) observed. Other studies have observed nonlinear relationships between N_2O emissions and N fertiliser rate (McSwiney and Roberston, 2005; Hoben et al., 2011).

In this study, N_2O emissions were measured from spring barley after fertiliser applications of CAN and urea with and without N stabilisers. Nitrogen stabilisers are fertiliser additives that reduce environmental N losses thereby stabilising the N in the soil. These can either a) reduce urea N loss via volatilisation and are termed urease inhibitors or b) reduce N loss via denitrification of nitrate and are termed nitrification inhibitors. These N stabilisers can thus increase fertiliser use efficiencies by increasing plant N uptake and crop yields. The N stabilisers evaluated in this study were the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT (trade name Agrotain™) and also referred to as n-BTPT in other studies), the nitrification inhibitor dicyandiamide (DCD), and the Maleic-Itaconic acid Co-polymer (MICO (trade name NutriSphere-N®)) which is a urease and nitrification inhibitor. The aims of this study were to quantify the effect of N fertiliser rate and formulation on direct N_2O emissions from spring barley in a temperate maritime climate and to develop crop

specific EFs for use in national N_2O emissions inventories. The hypothesis of this study is that changing N fertiliser source from CAN to stabilised urea reduces N_2O emissions.

4.3 Materials and Methods

4.3.1 Site description

Field plot trials were conducted on spring malting barley on a free-draining loam soil located in Marshalstown (MT), Co. Wexford. Site location and soil physical and chemical properties are described in Table 3.1 in chapter 3. This field site was located within the main malting barley growing region in Ireland (Duffy et al., 2015) and was representative of the typical soil type used for arable cropping. The site history was long term arable production for at least 20 years with continuous spring barley production since 2007.

4.3.2 Crop husbandry

The spring barley (*Hordeum vulgare* L.) cultivar used was 'Sebastian'. The site was ploughed (20 - 30cm depth) in February 2013 and March 2014. The crop was sown in mid-April in both years and was harvested in mid-August in both years. The experiment ran from April 2013 to April 2015 and generated emission factors for two years (crop sowing time to the following sowing time each year). The site characteristics are described in Table 3.1 in chapter 3 and are based on the top 10 cm of soil which is the standard agronomic soil sampling depth in Ireland. Each year basal phosphorus (P), potassium (K) and sulphur (S) were applied to the soil, according to the Teagasc Green Book of nutrient advice (Coulter and Lalor, 2008) to prevent nutrient deficiencies from occurring. A robust pesticide programme was applied to the crop to control weeds, pests and diseases as per standard agronomic practice for spring barley crops (Teagasc, 2016b).

4.3.3 Experimental Design

A randomised block design was used with five replicates of each fertiliser formulation. In addition to the unfertilised control, six fertiliser formulations were used: (i) CAN, (ii) urea (iii) urea + NBPT (iv) urea + DCD (v) urea + NBPT + DCD, and (vi) urea + MICO included in 2014 only. All fertiliser formulations were applied at the common N rate of 150 kg N ha^{-1} as this was the recommended N rate for spring barley as per the target crop yield. CAN and urea were applied at additional rates and details of the N fertiliser rates used are shown in Table 4.1. Each experimental unit (trial plot) measured 6m by 2.5m. Fertiliser was applied in two splits for all treatments. The first split comprised 30 kg N ha^{-1} and was surface applied within seven days of sowing. The second split was comprised of the remaining N fertiliser to make up the individual treatment rate (for 150 kg N ha^{-1} the 2^{nd} split was 120 kg N h^{-1}) and was applied during early to mid-tillering (Zadoks GS 20-25). The first split fertiliser was applied 15^{th} April 2013 and the 23^{rd} April 2014. The second split was applied 13^{th} May in both years. Pre-weighed fertiliser was applied by hand to the chamber base separately to the plot area to ensure the correct N application rate within the chambers.

Table 4.1 Nitrogen fertiliser formulations and rates for N_2O measurement

	N Rate (kg N ha^{-1})				
Fertiliser Formulation	**100**	**125**	**150**	**175**	**200**
CAN	✓	✓	✓	✓	✓
Urea	✓	✓	✓		✓
Urea + NBPT			✓		
Urea + DCD			✓		
Urea + NBPT + DCD			✓		
Urea + MICO			✓		

4.3.4 Soil and Climatic Analysis

Total daily rainfall, air temperature and humidity were recorded at a weather station adjacent to the site. Atmospheric pressure from the nearest available weather station at Johnstown Castle was used. Soil moisture was recorded on each day of N_2O measurement to a depth of 10 cm using a Delta T ML2 probe (Delta-T Devices, Burwell, Cambridge, UK). In addition to this, soil samples were taken on a weekly basis at the beginning of the year and on each day of measurement once the frequency of N_2O measurement was reduced later in the growing season. The gravimetric water content (GWC) of the soil was measured using these soil samples. Soil samples were taken to 10 cm depth using a soil corer (2 cm diameter). Five cores were taken from each plot, bulked together in sealed plastic bags and placed in a cool-box. Following sampling (i.e. within 2 hours) the soil samples were taken to the laboratory where they were wet sieved to 2 mm followed immediately by mineral N extraction using 2*M* potassium chloride (KCl) (1:5 ratio of soil to KCl) (Keeney and Nelson, 1982; Mulvaney, 1996). The mineral N extracts were analysed colorimetrically using an Aquakem 600A (Aquakem 600A, 01621, Vantaa, Finland) to determine the concentration of the mineral N species i.e. Total Oxidised N (TON (including nitrite (NO_2^-) and nitrate (NO_3^-)) and ammonium-N (NH_4^+-N). Soil sampling and mineral N extraction occurred weekly at the beginning of the experiment and was reduced to once fortnightly coinciding with the frequency of N_2O measurements. The gravimetric water content (GWC) of the soil samples was also measured on each day of sampling. Soil bulk density was measured four times over the course of the experiment (after the crop was planted and after harvest) and this was used with GWC to calculate volumetric water content (VWC). Soil bulk density and VWC were used to calculate water filled pore space percentage (WFPS %)

4.3.5 Nitrous oxide (N_2O) sampling and analysis

Daily N_2O fluxes were measured using the static chamber technique (Smith et al., 1995; Chadwick et al., 2014), adhering to the methodology guidelines compiled by the Global Research Alliance (de Klein and Harvey, 2012). The N_2O chamber measurement area was $0.4m^2$. Collars were installed to at least 5 cm into the soil (Smith et al., 2012) and contained a neoprene filled channel in order to maintain an air-tight seal. Collars were installed at least three days prior to the first sampling and were left in place for the duration of the study. Collars were removed for harvest and ploughing events and then reinstalled afterwards. When sampling, a stainless steel lid was placed onto the collar and a 10 kg weight was placed on top to compress the neoprene gasket, thus ensuring an airtight seal inside the chamber (plate 4.1). There were two different chamber sizes. A chamber with air volume 0.017 m^3 (10cm height) was used from sowing until Zadoks GS 32 - 33 (stem extension) (plate 4.2). Subsequently, larger chambers with an air volume of $0.096m^3$ (60cm height) were used until harvest (plate 2), after which small chambers were used again. Chambers were sampled prior to fertilisation, and then on a reducing temporal resolution for four weeks after fertiliser was applied i.e. four times per week for the first two weeks, twice per week for the next two weeks, and once per week thereafter. This sampling frequency was adopted to capture the period of most active N loss in more detail. In Year two, N_2O sampling was reduced to once every three weeks (after the initial four weeks of sampling after fertilisation) after reviewing year one data. The chamber lids were left on for 40 minutes, (larger chamber lids were left on for 60 minutes), then a 10 ml sample was taken from each chamber and immediately injected into a 7 ml pre-evacuated exetainer (Sigma-Aldrich, UK) fitted with double wadded septa (Labco, High Wycombe, UK). On each sampling date eight samples of ambient air were taken around the site and the average used as time zero (T0) sample for each chamber. Chadwick et al. (2014) have shown that

ambient samples are a useful surrogate for individual chamber T0 samples. On each sampling day, five chambers were chosen at random to check for linearity. These chambers were sampled at T0, T15, T30, T40, T60 and samples were statistically analysed to test for flux/no flux, quadratic or linearity. On each sampling day two sampling vials were injected with 0.5 ppm N_2O standard from the laboratory to ensure the integrity of samples during storage. Samples were analysed for N_2O using an electron capture detector (ECD) at 300°C. A CTC Analytics Combi-pal auto sampler (CTC Analytics, Industriestrasse 20, Zwingen, Switzerland) was used to inject gas samples into the Bruker Gas Chromatograph (Bruker, Bremen, Germany) (plate 4.3). Evolved N_2O was expressed as parts per million by volume (ppmv) having allowed for ambient concentrations and up-scaled to a flux in g N_2O-N ha^{-1} d^{-1} using equation 4.1 adapted from de Klein and Harvey (2012).

$$F_{N2O} = (\partial c/\partial t) * ((M * P)/R * T)) * (V/A)$$

Equation 4.1 Calculating N_2O emission in g N_2O-N ha^{-1} d^{-1}

Where:

∂c is the change in gas concentration in the chamber headspace during the enclosure period (ppbv), ∂t is the enclosure period expressed in minutes, M is the molar mass of N_2O-N (28 g mol^{-1}), P is atmospheric pressure (Pa) at the time of sampling, T is the temperature (K) at the time of sampling, R is the ideal gas constant (8.314 J k^{-1} mol^{-1}), V is the headspace volume of the chamber and A is the area covered by the chamber (ha).

Sampling occurred between 10 am and 2 pm each day as per Chadwick et al. (2014). The limit of detection of the method was calculated by averaging the standard deviation of all ambient samples for each year and then subtracting three standard deviations. This was 0.26 ppm and 0.28 ppm for 2013 and 2014, respectively. Anything below this was

excluded from the study. In total over the two years 39 data points were removed as limits of detection out of a total of 5980 data points.

Plate 4.1 Stainless steel lid placed on top of collar for measuring N_2O emissions with a 10kg weight to ensure an airtight seal

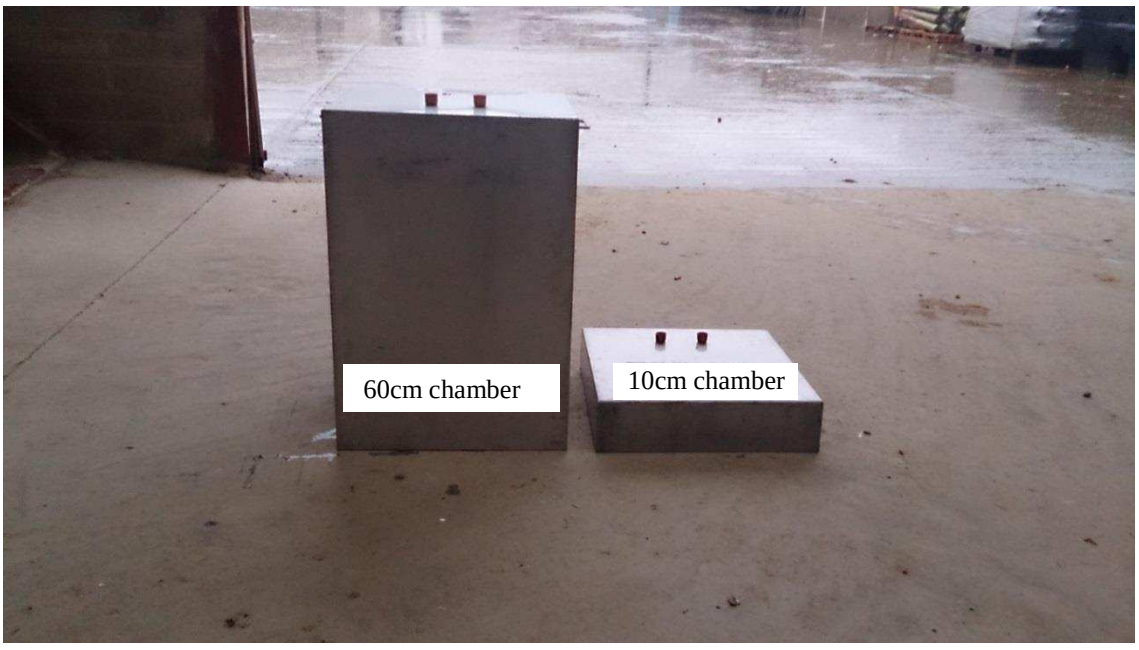


Plate 4.2 10cm N_2O chamber used for measuring N_2O emissions from sowing until zadoks GS 32 - 33 and after harvest and 60cm N_2O chamber used for measuring N_2O emissions from zaddoks GS 32 - 33 until harvest

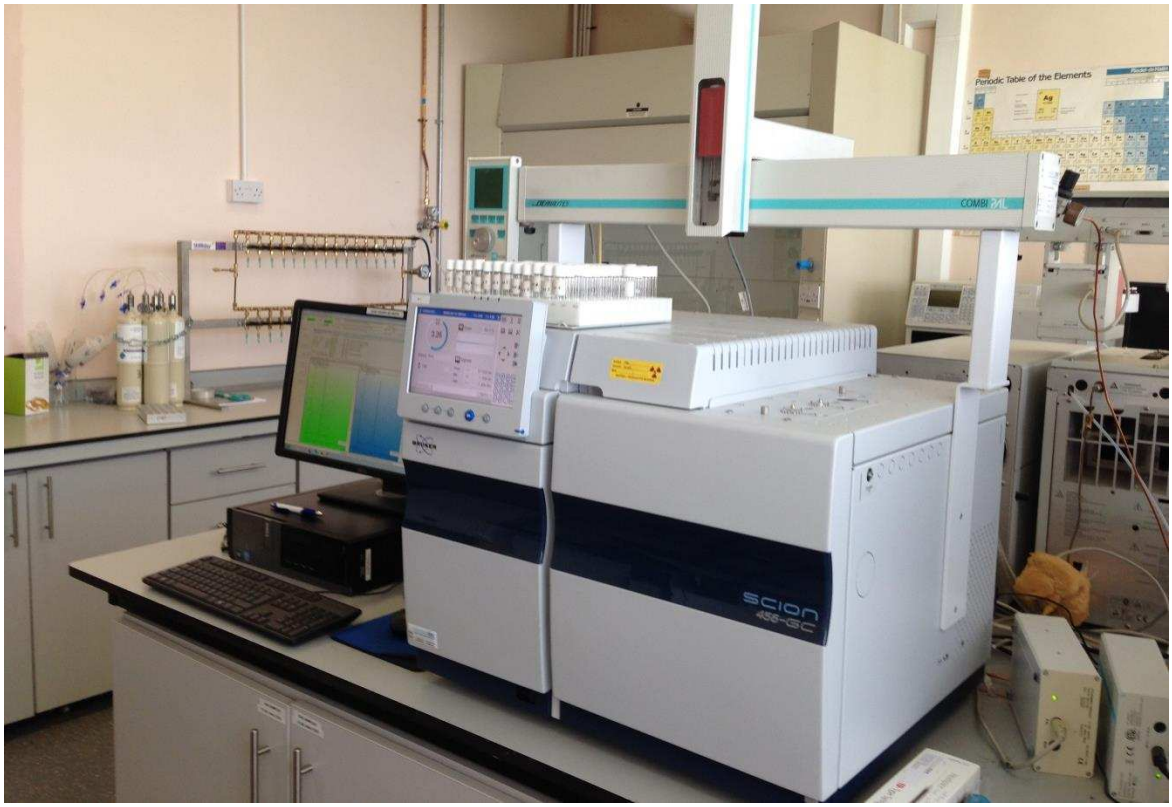


Plate 4.3 Combi pal autosampler attached to the bruker gas chromatograph for analysing N_2O samples

4.3.6 Emission Factor calculation

Cumulative N_2O fluxes from each chamber were calculated using trapezoidal integration to interpolate fluxes between sampling dates. Trapezoidal integration was used to linearly integrate fluxes from one sampling day to the next sampling day in order to generate fluxes for 365 days in order to generate cumulative fluxes. For each formulation, cumulative fluxes were calculated using the mean of the five replicates. The EFs were then calculated using equation 4.2.

$$EF\ (\%) = \frac{N_2O\text{-}N\ cumulative\ (formulation) - N_2O\text{-}N\ cumulative\ (unfertilised\ control)}{Fertiliser\ N\ applied} \times 100$$

Equation 4.2 Equation for calculating N_2O emission factors

Annual EFs were calculated over a 365 day period (IPCC, 2006). As calendar year (January – December) measurement is not appropriate for tillage systems, EFs were calculated from sowing date to the subsequent years sowing date and normalised to 365 days. Nitrous oxide yield efficiency was calculated by dividing the cumulative N_2O-N ha^{-1} (kg) of a treatment by the grain yield (t ha^{-1}) for the same treatment which produced N_2O yield efficiency (kg N_2O-N t^{-1} grain).

4.3.7 Linearity of N_2O flux

Results from the randomly selected N_2O chambers, used to assess if the N_2O flux was linear, showed on average linear accumulation. Initial analysis of this data was conducted to assess if a flux in N_2O emissions occurred. In some cases there was no flux evident (Table 4.2). The chambers showing N_2O flux were then analysed for linear or quadratic accumulation of N_2O. Over 90% of these chamber measurements in both sites in both years showed linear accumulation according to the criteria of Chadwick et al. (2014) (Table 4.2). This shows that the assumption of linear accumulation in the headspace can be used. This is in agreement with work conducted by Chadwick et al. (2014) where over 90% of chamber measurements (n=1970) from multiple field experiments, showed linear N_2O accumulation.

Table 4.2 N_2O linearity samples for 2013 and 2014

	2013	**2014**
Total No. chambers	260	212
Chambers without N_2O flux	212	73
Chambers with N_2O flux	48	139
Of chambers with flux	**%**	
Quadratic	**8**	**6**
Linear	**92**	**94**

4.3.8 Statistical Analysis

Statistical analysis was conducted using the PROC GLIMMIX and PROC MIXED procedures in SAS 9.3 (2002-2010, SAS Institute Inc., Cary, NC, U.S.A.). PROC MIXED was used to conduct a repeated measures analysis of variance (ANOVA) of the temporal N_2O and mineral N data. Residual graphs were generated to check for normality. Log transformation of all temporal data was conducted as there was high variability within the dataset and nonconformity with the assumptions about normality in ANOVA. Residual influence statistics were used to identify potential outliers and showed which data points were the most influential on the entire dataset. These 'potential outliers' were then assessed to check if they were genuine outliers. The assessment of the temporal N_2O data identified only six individual flux measurements that were 'genuine outliers'. These were subsequently removed from the dataset and the average of the other four replicates was then used for that day for gap-filling to generate the cumulative flux. The PROC GLIMMIX procedure was used to test for treatment differences in cumulative emissions. Significant differences were determined according to the F-protected least significant difference test ($P < 0.05$).

Dixons test was used to identify outliers in the ambient data. The minimum detectable flux was then calculated according to Appendix 2 in the chamber methodology guidelines (de Klein and Harvey, 2012). Repeatability, standard deviation and repeatability limit was calculated as per (Ellison et al., 2009). The minimum detectable flux (MDF) was calculated to be 2.59 and 7.78 g N_2O-N ha^{-1} day^{-1} in 2013 for small and large chambers, respectively. In 2014 the MDF was calculated to be 2.86 and 7.84 g N_2O-N ha^{-1} day^{-1} for small and large chambers, respectively.

4.4 Results

4.4.1 Soil and Climatic conditions

The weather during the experiment was typical of the weather for this region with most of the rainfall occurring during the autumn and winter months and the highest temperatures occurring during the summer months (Figure 4.1a and 4.2a). In both years, the highest average daily temperature was 17°C in July and the highest total monthly rainfall was in October with 189 mm in 2013 and 173mm in 2014. Total monthly rainfall and average temperature were higher in April (68.4mm) and May (74.8mm) in 2014 compared with April and May 2013 with 47.2mm and 53.6mm and the national 30 year average with 59.1 and 55.7mm for April and May respectively. Water filled pore space ranged from 15.74% - 66.09% in 2013 and 28.6% - 68.2% in 2014 with the lowest WFPS% occurring in the summer months. Soil total oxidised nitrogen (TON) and ammonium (NH_4^+) concentrations increased after fertiliser application (Figure 4.1b and 4.2b). Elevated soil TON levels occurred following the 2nd split application of CAN. In 2013, levels reached 95.2 mg TON kg^{-1} soil two days post-application and 106.8 mg TON kg^{-1} soil 24 days after application for CAN. After this TON levels from CAN were reduced to below 50 mg TON kg^{-1} soil. In

2014, TON levels from CAN reached 190 mg TON kg^{-1} soil three days after application. Generally, all other fertiliser formulations had lower TON levels than CAN. Urea + DCD and urea + NBPT + DCD levels were similar to the unfertilised control levels. The highest NH_4^+ concentration in 2013 was 161.13 mg NH_4^+ kg^{-1} soil (urea + NBPT + DCD) and in 2014 was 257.98 mg NH_4^+ kg^{-1} soil (urea + DCD). All fertiliser formulations produced an NH_4^+ peak after application but CAN produced the highest TON peak.

4.4.2 N_2O emissions: fertiliser formulation and N stabilisers at 150 kg N ha^{-1}

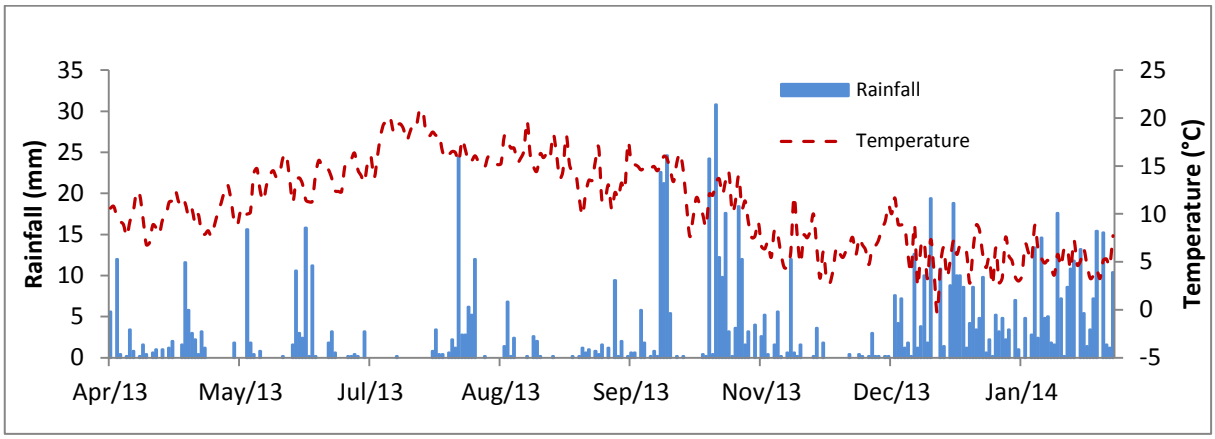
Nitrous oxide emissions increased from background levels post-fertiliser application with the highest observed fluxes of 44 g N_2O-N ha^{-1} d^{-1} in 2013 (Figure 4.1c) and 43g N_2O-N ha^{-1} d^{-1} in 2014 (Figure 4.2c). This peak in N_2O emission corresponded closely with timing of fertiliser application and rainfall occurring 15 and 13 days following the main fertiliser split application in 2013 and 2014 respectively. The association of N_2O emissions with fertiliser application was most pronounced following the second fertiliser application of 120 kg N ha^{-1}. The initial split was 30 kg N ha^{-1} and resulted in a lower quantity of N_2O loss.

In 2013 the largest daily fluxes came from urea, CAN, and urea + NBPT, in that order. The profile of temporal emissions from urea + DCD and urea + NBPT + DCD were similar to the unfertilised control. Approximately 16 weeks after fertiliser application, emissions returned to background levels (i.e. similar to that of the unfertilised control) and remained so for the remainder of the year in 2013 for all formulations.

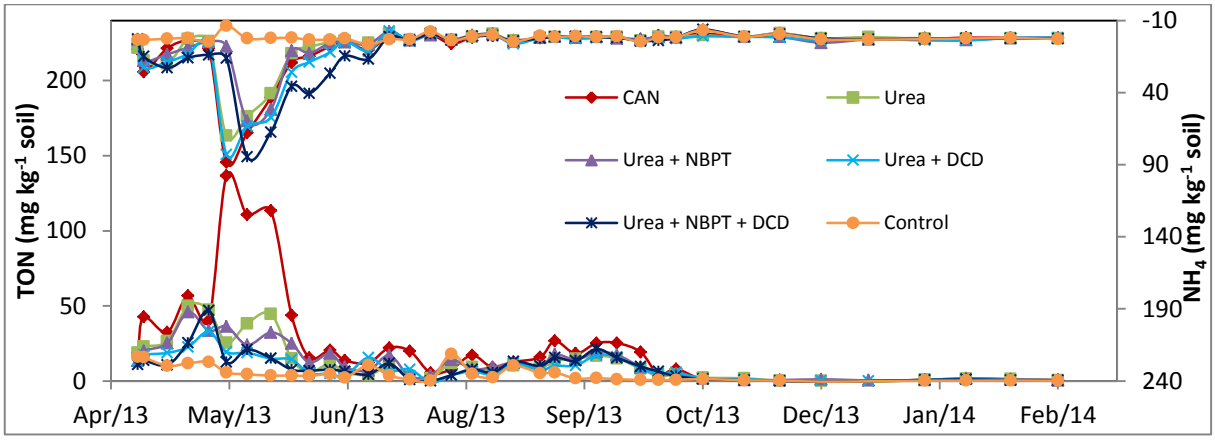
In 2014 there was a peak in emissions after fertiliser application with the largest daily fluxes from CAN, urea + NBPT and urea in that order. Approximately four to six weeks

after the second split fertiliser application emissions returned to background levels and remained so for the remainder of the year for all formulations.

(a)



(b)



(c)

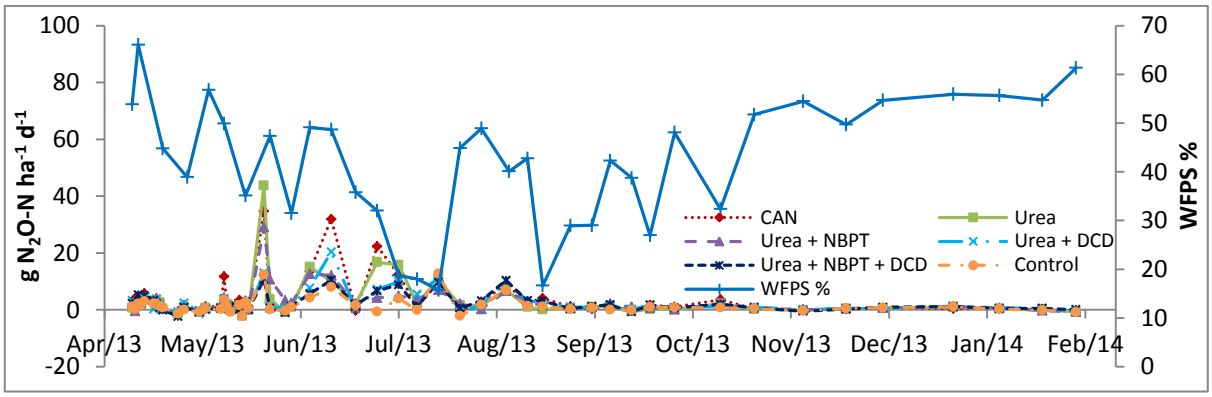
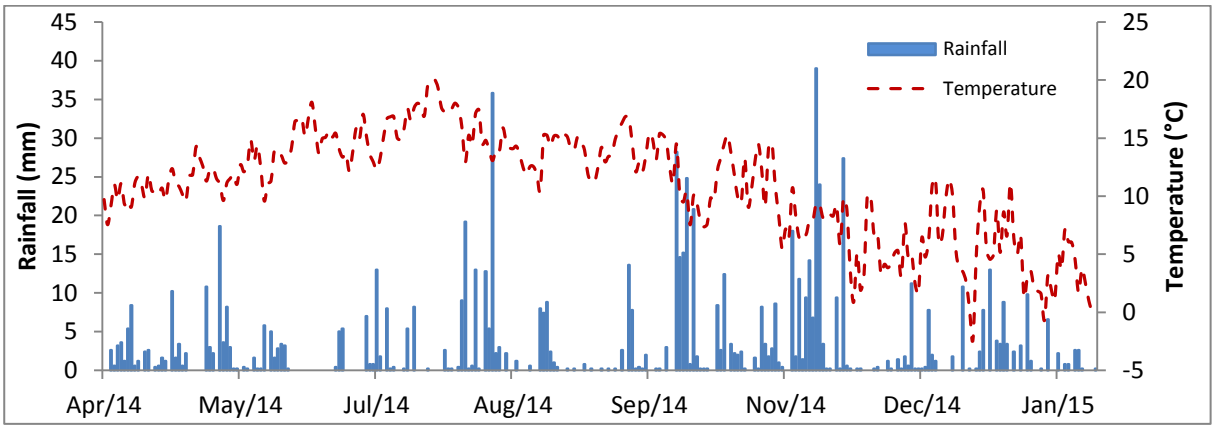


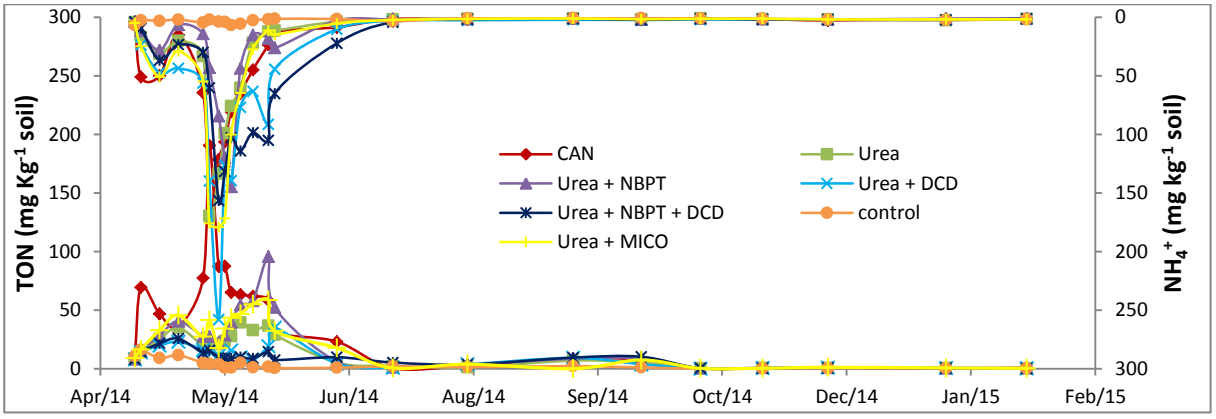
Figure 4.1 2013 temporal emissions data (a) total daily rainfall (mm) and daily average temperature (°C) and, (b) daily soil mineral N concentrations (0–10 cm) and, (c) daily N_2O emissions in g N_2O-N ha^{-1} day^{-1} and Water Filled Pore Space percentage (WFPS %)

*arrows represent fertiliser application @ 150 kg N ha^{-1}

(a)



(b)



(c)

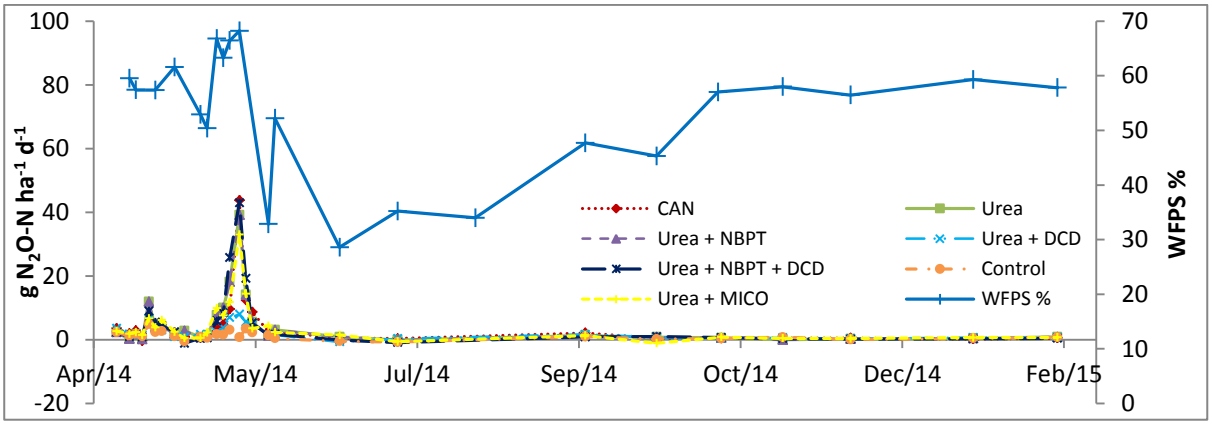


Figure 4.2 2014 temporal emissions data (a) total daily rainfall (mm) and daily average temperature (°C) and, (b) daily soil mineral N concentrations (0–10 cm) and, (c) daily N_2O emissions in g N_2O-N ha^{-1} day^{-1} and Water Filled Pore Space percentage (WFPS %) *arrows represent fertiliser application @ 150 kg N ha^{-1}

4.4.3 Cumulative emissions and emission factors

Cumulative N_2O emissions were all below 0.5% across all formulations and years. In both years CAN produced significantly higher emissions than the unfertilised control with 1161 g N_2O-N ha^{-1} in 2013 and 513 g N_2O-N ha^{-1} in 2014 (Table 4.3) compared with 424 g N_2O-N ha^{-1} from the control in 2013 and 191 g N_2O-N ha^{-1} from the control in 2014. In 2013 N_2O losses from CAN, urea and urea + DCD were not significantly different. Urea + NBPT and urea + NBPT + DCD had significantly lower emissions compared to CAN and were also not significantly different to N_2O emissions from the unfertilised control. In 2014 urea + DCD was the sole fertiliser formulation which had significantly lower N_2O loss compared to CAN, urea and urea + MICO. Emission factors ranged from 0 – 0.49% with the numerically highest EF of 0.49% from CAN in 2013. CAN and urea had the highest direct EFs in each year and all EFs were lower than the IPCC default of 1% regardless of formulation. Urea + NBPT + DCD had the lowest EF in 2013 and urea + DCD had the lowest EF in 2014 and the lowest mean EF.

Table 4.3 Cumulative direct N_2O emissions in g N_2O-N ha^{-1} and emission factors for 2013 and 2014

	2013		2014		Average
Fertiliser Formulation	**Cumulative Emissions g N_2O-N ha^{-1}**	**Emission Factor (%)**	**Cumulative Emissions g N_2O-N ha^{-1}**	**Emission Factor (%)**	**Emission Factor (%)**
CAN	1161a	0.49	513a	0.21	0.35
	(166)		(94)		
Urea	889ab	0.31	538a	0.23	0.27
	(45)		(99)		
Urea + NBPT	772bc	0.23	427ab	0.16	0.20
	(173)		(41)		
Urea + DCD	804ab	0.25	191b	0	0.13
	(140)		(62)		
Urea + NBPT + DCD	723bc	0.20	364ab	0.12	0.16
	(105)		(105)		
Urea + MICO	N/A		455a	0.18	0.18
	N/A		(176)		
Control	423c		191b		
	(57)		(95)		

*Different letters represent significant differences between treatments for cumulative emissions using F protected LSD test ($P<0.05$) and comparisons are within each year

*Treatment SE (standard error) for each treatment at each site shown in brackets.

4.4.4 Impact of fertiliser rate on N_2O emissions

The impact of N rate (100-200 kg N ha^{-1}) on EF_1 was unclear. There was no significant impact of application rate on the CAN EF in either year as evidenced by the lack of a significant correlation between the EF and N rate (Table 5). However, a significant negative correlation between N rate and the urea EF was observed in 2013 but not in 2014 (Table 5). The model that best fitted this equation was quadratic with an r^2 value of 0.96; the equation of the line is presented in Table 4.4.

Table 4.4 Effect of N rate on N_2O emission factors for CAN and urea

Treatment	**P value (slope different to zero)**	**Equation***
CAN 2013	0.258	N/A
Urea 2013	0.0321	$y = 8E\text{-}05x^2 - 0.0287x + 2.8594$
CAN 2014	0.225	N/A
Urea 2014	0.0811	N/A

***y = Emission factor and x = N fertiliser rate

4.4.5 N_2O yield efficiency

Nitrous oxide yield efficiency ranged from 0.09 – 0.16 kg N_2O-N t^{-1} grain in 2013 and 0.02 – 0.07 kg N_2O-N t^{-1} grain in 2014. There were no significant differences between fertiliser formulations in either year but there were differences between the unfertilised control and fertiliser treatments (Figure 4.3). In 2013, the unfertilised control was significantly higher than all fertiliser treatments with 0.16 kg N_2O-N t^{-1} grain except for CAN and in 2014 the unfertilised control was higher than urea + DCD with 0.05 kg N_2O-N t^{-1} grain and not different to any other treatment.

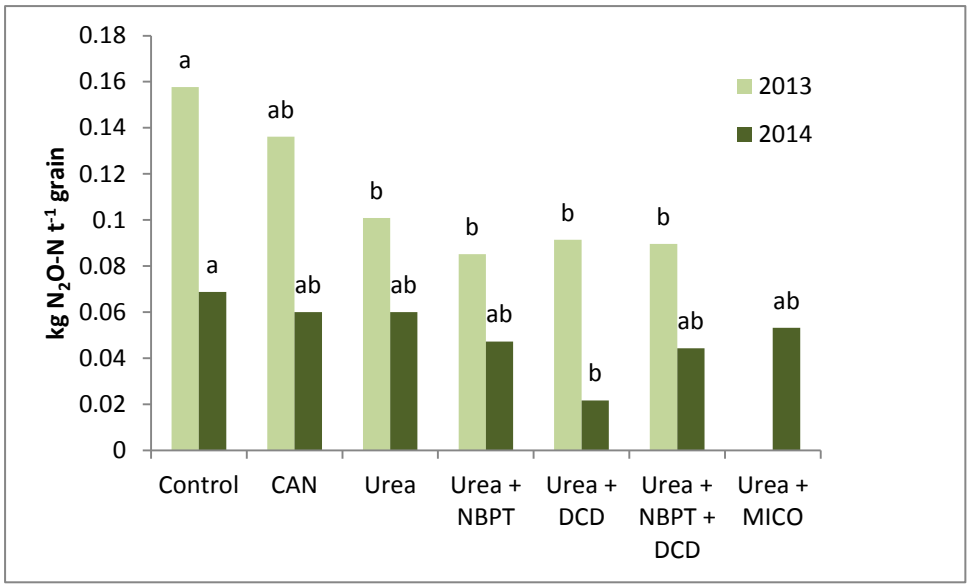


Figure 4.3 N_2O yield efficiency (kg N_2O-N t^{-1} grain) for 2013 and 2014

*Different letters represent significant differences between treatments using F protected LSD test ($P<0.05$) and comparisons are within each year

4.5 Discussion

4.5.1 Effect of environmental factors on N_2O emissions

The application of N resulted in a peak in soil mineral N concentrations with CAN producing significantly higher NO_3^- peaks compared to other N forms and all fertiliser formulations producing NH_4^+ peaks. This study showed that using a urea based fertiliser reduced the soil NO_3^- pool compared to CAN. Thus, there is less TON for denitrification and leaching from the urea based fertilisers. The soil NH_4^+ pool was similar regardless of the N formulation used.

Whilst rainfall and temperature at the time of fertiliser application were higher in 2014 than in 2013, cumulative emissions were lower in 2014 compared with 2013. In 2013 there were multiple emission peaks resulting in higher cumulative emissions whereas in 2014 there was one main peak after each fertiliser application. The slightly lower levels of N_2O in 2014 could indicate that either complete denitrification occurred producing N_2 instead of N_2O (Focht et al., 1979), or that the nitrate was leached due to higher rainfall events combined with the free-draining soil texture, or that more N was taken up by the crop due to less drought stress.

In general, cumulative emissions were low ranging from 191 g N_2O-N ha^{-1} yr^{-1} to 1161 g N_2O-N ha^{-1} yr^{-1} and with EF_1 ranging from 0 to 0.49%. This is consistent with previous studies on spring barley sites in Ireland, where EF for CAN during the growing season (not full year) was observed to be 0.5% (Abdalla et al., 2010). The relatively low EF_1 could be explained, in part, by the soil characteristics. The soil was a free-draining cambisol with a C content of 2.88%, which is typical of Irish arable soils. In a meta-analysis of over 1000 studies, Stehfest and Bouwman (2006) concluded that N_2O emissions were significantly lower on soils with SOC <3% and Gilsanz et al. (2016) observed the lowest EFs in soil

textures with low clay content (less than 50%) and with sand content greater than 50%. In a study at three arable sites, the EF_1 for ammonium nitrate was observed to be substantially lower than the default value (0.2% and 0.33%) at two free-draining sites (Bell et al., 2015). In contrast, grasslands exhibit both higher mean emissions and a larger range in EFs (Harty et al., 2016a). Dobbie and Smith (2003a) reported EF_1 ranging from 1% - 3% in Scottish grasslands whilst previous studies on total N_2O losses in Irish grasslands (including N deposition form fertiliser (EF_1) and animal excreta (EF_3)) have exhibited a range from 0.7% to 7.7% (Hyde et al., 2006; Rafique et al., 2011; Li et al., 2011, Burchill et al., 2014).

4.5.2 Effect of fertiliser formulation and incorporation of N stabilisers on N_2O emissions

N_2O emission peaks in general corresponded with rainfall events and elevated soil TON and NH_4^+ concentrations. The majority of N_2O emissions occurred after the second and the larger split fertiliser application with the highest N_2O emissions and EFs associated with CAN and urea application. There were no significant differences in N_2O emissions between CAN and urea. A comparison between urea and ammonium nitrate (AN) at three UK sites also found no differences in N_2O emissions between fertiliser formulations, with higher emissions for both fertilisers at the site with highest rainfall (Bell et al., 2015). Similarly, Louro et al. (2015) reported no significant fertiliser formulation effect on N_2O emissions. In contrast, Dobbie and Smith (2003a) observed lower N_2O emissions associated with urea application compared to ammonium nitrate (AN). This effect was season dependant with no differences when fertiliser was applied in late summer. The findings from this study suggest that the addition of the nitrification inhibitor DCD to urea has potential to reduce N_2O emissions by 30% compared to CAN. The inhibitory effect of DCD can vary depending on climate and soil conditions as well as vegetation type (Gilsanz et al., 2016) and is likely to be more effective where there are higher losses such as wetter

soils. Bell et al. (2015) observed a decrease in the EF_1 for AN from 0.55% to 0.06% upon application of DCD. In addition, Dobbie and Smith (2003a) observed a 50% reduction in cumulative emissions using urea + DCD compared to urea alone, but observed no benefit of urea + NBPT on direct N_2O emissions. The potential effects of DCD uptake by the plant and contamination in crop off takes is needed as recently highlighted in New Zealand (Pal et al., 2016). In studies with higher emissions the inclusion of a urease inhibitor with urea reduced N_2O emissions compared with CAN (McTaggart et al., 1997). While NBPT treated urea did not reduce direct N_2O emissions compared to urea in this study, inclusion of NBPT with urea has been shown to reduce volatilisation from urea (Watson et al., 2009; Forrestal et al., 2015) which will reduce indirect N_2O emission associated with the deposition of atmospheric NH_3 (Asman et al., 1998). Urea + MICO showed no effect on N_2O emissions compared to CAN or urea. This corresponds with the literature which shows that urea + MICO is not an effective nitrification or urease inhibitor (Chien et al., 2014; Franzen et al., 2011., Goos, 2013). The EFs for all fertiliser formulations were <50% of the IPCC default value of 1%. Against this background these fertiliser formulations appear to have similar N_2O loss potential in spring barley which tends to be cropped to free draining sites similar to this study. Other studies on arable land in similar climates have also shown EFs lower than the IPCC default (Abdalla et al., 2010; Bell et al., 2015).

The N_2O yield efficiency was highest for the unfertilised control but there were no differences between fertiliser formulations which is in agreement with Hinton et al. (2015). It's important to account for crop yield as well as N_2O emissions when assessing fertiliser formulations to determine if they are economically viable (Hinton et al., 2015). This study showed similar N_2O yield efficiency regardless of the fertiliser formulation used.

4.5.3 Effect of N rate on N_2O emissions

There was no EF response to rate of N application for CAN and urea in 2014. Bell et al. (2015) also observed no consistent increase in EF_1 in response to increased rate of AN applied to arable cropped soils. In the current study there was a negative correlation observed between EF_1 and rate of urea application 2014, with EF_1 0.7% at the lowest N application (100 kg N ha^{-1}) compared to 0.4% at the highest N application (200 kg N ha^{-1}). This may be related to higher ammonia volatilisation occurring at higher N fertiliser application rates (Black et al., 1985; Van der Weerden and Jarvis, 1997). The negative or lack of correlation between EF_1 and applied N rate in the present study indicates that higher NH_3 loss may have taken place and this could result in reduced yields which have been observed in previous studies (Devine and Holmes, 1963; Gately, 1994; Conry et al., 1997). The addition of NBPT protects against this NH_3 loss with reductions of 78.5% on average measured in Irish grassland (Forrestal et al., 2015).

4.5.4 Emission Factors and comparison to IPCC default

Over the two year period of the study the EFs from all fertiliser formulations ranged from 0% (from urea + DCD in 2014) - 0.49% (from CAN in 2013). Other studies on UK soils have shown higher EFs from AN than those observed from CAN in this study (Dobbie et al., 1999; Hinton et al., 2015). The fact that the highest EF recorded (0.49%) was half the magnitude of the IPCC 1% default, highlights the potential importance of countries moving to a Tier 2 methodology using system specific data to generate more accurate N_2O emission inventories. Further research is required in order to determine the appropriateness of the use of the default EF in other scenarios such as different land use types. Furthermore the use of nitrification inhibitors significantly decreased the observed EF. While the use of urease inhibitors did not lead to significant reductions in direct N_2O EFs, potential

reductions in ammonia volatilisation as a result of urease inhibition could significantly reduce indirect N_2O losses associated with the redeposition of atmospheric ammonia (EF_4).

4.6 Conclusions

Overall, N_2O emissions from the fertilisers tested in this study were less than half the IPCC default value of 1%. The lack of a clear relationship between fertiliser rate and direct N_2O emissions questions the appropriateness of the IPCC default values on soils with low emissions in temperate conditions. This site is representative of the soil type for the majority of spring barley in Ireland and so, based on this study, it is likely that N_2O emissions from the majority of spring barley in Ireland are below the IPCC default value. In terms of fertiliser form, it is important to account for indirect emissions from NH_3 volatilisation when calculating EFs upon switching from ammonium nitrate to urea-based fertiliser forms, as otherwise total emissions associated with N application will be underestimated. The present research emphasises the importance of developing country and system specific emission factors to better estimate greenhouse gas emissions from agriculture.

Chapter 5 - Impact of fertiliser nitrogen formulation and N stabilisers on nitrate leaching in spring barley

5.1 Summary

The application of synthetic N fertilisers to agricultural soils contributes to environmental losses of N including NO_3^- leaching to waterbodies. Nitrate leaching can contribute to eutrophication of waterbodies and can cause human health problems. Nitrate leaching also represents an economic loss of N from the farm. Under the Water Framework Directive (WFD) and the Nitrates Directive (ND), Ireland is obliged to limit NO_3^- in drinking water to 50 mg NO_3^- L^{-1} (NO_3^--N to 11.3 mg L^{-1}). Nitrate leaching losses from arable land can be substantial particularly during the winter period when the land is left fallow, as there is no crop N uptake to capture available N. The dominant N fertiliser used in Ireland is CAN which contains 27% N, half in the NO_3^- form which can immediately contribute to NO_3^- leaching losses under favourable weather conditions. Nitrogen stabilisers can be added to urea fertiliser to slow down the N transformation processes in soil and could potentially reduce NO_3^- leaching losses compared to CAN. The objectives of this study were: (1) to quantify the effect of CAN, urea and urea stabilised with NBPT + DCD on NO_3^- leaching losses, and (2) to assess the effect of different N rates of CAN (ranging from 100 - 200 kg N ha^{-1}) on NO_3^- leaching. Results showed that fertiliser formulation had no significant effect on NO_3^- leaching losses and urea + NBPT + DCD produced similar levels to CAN. There was a significant effect of N rate on leaching losses with the highest losses from CAN at application rates of 150 kg N ha^{-1} and 200 kg N ha^{-1} respectively.

5.2 Introduction

The use of synthetic N fertilisers for intensive agricultural systems contributes to losses of reactive N (Nr) and these Nr losses are of considerable environmental concern (Sutton et al., 2011). Losses of Nr to the environment are damaging for air quality contributing to greenhouse gas emissions as discussed in chapter four (nitrous oxide chapter) and is also damaging to water quality. One of the major sources of Nr contributing to reduced water quality is NO_3^- leaching from agricultural systems to waterways (Shepherd and Lord, 1996; Bjorneberg et al., 1996; Di and Cameron, 2002a). Leaching of NO_3^- to waterways can contribute to eutrophication (Stark and Richards, 2008) and human health problems (Knobeloch and Salna, 2000; Ward et al., 2005) and this loss of NO_3^- from the soil also represents an economic loss to farmers. It is expected that the anthropogenic addition of Nr to the environment will increase with increased global population and food demand (Gruber and Galloway, 2008) but this increase should be curtailed by national and international legislation aimed at managing N inputs to agriculture more sustainably.

There are several forms of legislation for the protection of water quality against pollution. The World Health Organisation (WHO) introduced a drinking water limit for NO_3^- levels of 50 mg NO_3^- L^{-1} and the EU drinking water limit is also 50 mg NO_3^- L^{-1} or 11.3 mg NO_3-N L^{-1}. The EU also introduced the ND, Good Agricultural Practices for Protection of Waters, for the protection of waters against agricultural pollution. The ND has been in place since 1991 and it aims to protect ground and surface water quality from pollution from agricultural sources. All EU member states are required to prepare nitrates action programmes (NAPs) that ensure adherence to the directive and the protection of water quality. Irelands latest NAP includes maximum allowable N fertilisation rates and closed periods where the application of N (and phosphorus) fertilisers and organic manures are prohibited. Farmers across the EU must adhere to the rules set out in the ND legislation in

relation to the management of N on their farms. The ND is part of the overarching Water Framework Directive (European Communities, 2000 (2000/60/EEC)) whose objectives are to protect the aquatic environment and sets out targets for water quality across the EU.

For the tillage sector most of the N losses originate from the use of synthetic N fertilisers. Arable land in Ireland accounts for approximately 10% of the total agricultural land (DAFM, 2012) and 46% of this is cropped with spring barley (CSO, 2016). Arable land can contribute to substantial NO_3^- leaching losses with studies showing up to 107 kg NO_3^- ha^{-1} $year^{-1}$ (Di and Cameron, 2002a) with up to 94 kg N ha^{-1} $year^{-1}$ on free-draining soil cropped with spring barley in Ireland (Hooker et al., 2008). Arable cropped land mostly uses synthetic N fertilisers which are generally split into two or three fertiliser applications in Ireland and so large quantities of N are applied with few application timings. If the N fertiliser application coincides with a heavy rainfall event and high drainage this could result in increased NO_3^- leaching losses. Although NO_3^- generally accounts for the highest proportion of N leaching, DON leaching is also an important N loss pathway (Van kessel et al., 2009) and studies have shown ammonium leaching losses to be negligible (Brown et al., 1982; Mancino and Troll, 1990).

The main N fertiliser source used by tillage farmers in Ireland is calcium ammonium nitrate (CAN) or ammonium nitrate based compounds. CAN comprises 27% N, 50% ammonium and 50% nitrate. Nitrate is an anion and is not retained on soil exchange sites and is thus easily leached. Research has highlighted that spring barley systems in Ireland can contribute significant NO_3^- leaching losses of between 3 and 51 kg N ha^{-1} (Thorn, 1986) and between 16 - 94 kg N ha^{-1} on free draining soils (Hooker et al, 2008). Thus, changes to fertiliser recommendations would need to be evaluated in terms of N leaching potential associated with changes in N fertiliser input rate and form. The NO_3^- in CAN may

also be lost as dinitrogen gas (N_2) or nitrous oxide (N_2O) through the processes of nitrification and denitrification (discussed in chapter 4).

Urea contains 46% N and this N must be first converted from urea to NH_4^+ and then converted from NH_4^+ to NO_3^- before fertiliser N leaching can occur. The application of CAN immediately contributes to the soil NO_3^- pool and therefore fertiliser N is immediately available for leaching processes. In addition, the NH_4^+ in CAN can be quickly converted to NO_3^- and also leached. When urea is applied to soil it hydrolyses to NH_4^+ and during this process ammonia gas can be released to the atmosphere. Some studies have showed reduced yields using urea compared to CAN (Devine and Holmes, 1963; Gately, 1994; Conry, 1997) and so urea is not commonly used for spring barley in Ireland. Urea can have elevated NH_3 emissions which is discussed in chapter 6.

The use of N stabilisers (also called inhibitors) has potential to reduce these N loss risks associated with urea and CAN. Urease inhibitors slow down the urea hydrolysis process and can reduce NH_3 emissions, whereas nitrification inhibitors slow down the nitrification process thereby reducing the size of the soil NO_3^- pool and reducing the potential N losses through N_2O emissions and NO_3^- leaching. Limited studies of N leaching on spring barley have been conducted. Thorn (1986) investigated NO_3^- leaching from spring barley fertilised with CAN by soil sampling at the end of the growing season and again at the beginning of the next growing season and found leaching losses of 3 – 51 kg N ha^{-1} with 55 – 129 kg N ha^{-1} applied. Hooker et al. (2008) found leaching losses of 16 – 94 kg N ha^{-1} from spring barley with an N application rate of 160 kg N ha^{-1}.

The effect of different N fertilisers including N stabilisers on NO_3^- losses from spring barley has not previously been studied in Ireland. The objectives of this study were to investigate the effect of N fertiliser type (CAN versus urea) on NO_3^- leaching and to

investigate the effect of N stabilisers for further reducing NO_3^- leaching from urea. The study hypothesis was: switching N fertiliser formulation will reduce NO_3^- leaching in spring barley and that increasing N fertiliser rate will increase NO_3^- leaching.

5.3 Materials and Methods

5.3.1 Site Description

Field experiments were conducted on a free-draining loam soil located in Marshalstown (MT), Co. Wexford and a moderately draining sandy loam soil located in Johnstown Castle (JC), in Co. Wexford. The sites locations and soil characteristics can be seen in Table 3.1 in chapter 3. Marshalstown has been in long term arable production for approximately 20 years with continuous spring barley production since 2007 and JC has been in arable production for six years. Prior to this, the JC site was permanent grassland until 2010 when it was cropped with maize for three years before spring barley. This site had received organic manure annually while it was managed for grassland and maize production. The last application of manure was in autumn 2012, prior to these experiments which started in spring 2014.

5.3.2 Crop husbandry

The spring barley (*Hordeum vulgare L*) cultivar was 'Sebastian' which is a Danish malting variety with short straw. The sites were ploughed (20 - 30cm depth) in March in 2014 and 2015. Spring barley seed from Boortmalt, Ireland was sown in April in both years and was harvested at maturity. This NO_3^- leaching study ran from April 2014 to April 2016 generating two years of N leaching data. The sites characteristics are described in Table 3.1 in chapter 3 and are based on the top 10cm of soil. Each year basal P, K and S were applied

to the soil, according to the Teagasc Green Book of nutrient advice (Coulter and Lalor, 2008) to prevent any nutrient deficiencies from occurring. A robust pesticide programme was applied to the crop to control weeds, pests and diseases as per standard agronomic practice for spring barley crops (Teagasc, 2016b).

5.3.3 Experimental Design

A randomised block design was used with four replicates of each treatment in JC (Figure 3.2 in chapter 3) and three replicates of each treatment in MT (Figure 3.3 in chapter 3). Lysimeters were installed in 2013 at both sites, 24 lysimeters were successfully installed in JC but there was difficulty installing lysimeters at the MT site and so only 16 lysimeters were installed in 2013. In 2014 two more lysimeters were installed so there were three replicates of each treatment. Lysimeters were left in place in 2013 and water was pumped out prior to the first measurements beginning in 2014. Five fertiliser formulations were evaluated and also an unfertilised control. The fertiliser formulations were (i) CAN @ 100 kg N ha^{-1}, (ii) CAN @ 150 kg N ha^{-1}, (iii) CAN @ 200 kg N ha^{-1}, (iv) urea @ 150 kg N ha^{-1}, (v) urea + NBPT + DCD @ 150 kg N ha^{-1}. The lysimeters were installed within spring barley plots that measured 12m x 2.5m. Fertiliser was applied in two split applications. The first split comprised 30 kg N ha^{-1} and was surface broadcast within seven days of sowing. The second split comprised the remainder fertiliser to make up the individual treatments (e.g.30 kg N ha^{-1} applied at the first split and 70 kg N ha^{-1} applied at the second split for 100 kg N ha^{-1} total application) and was applied during early to mid-tillering (also surface broadcast). Dates of fertiliser application for each site and each year are shown in Table 3.2 in chapter 3.

5.3.4 Lysimeter establishment

Lysimeters were established during January and February 2013. A single lysimeter unit consisted of a plastic cylinder with a 7 mm thick wall and was 215mm in diameter. To fill the lysimeter units, a digger was used to remove the topsoil (plough layer) from the area to reveal the subsoil (30cm depth). An intact soil core was extracted using a steel cutting unit (Plate 5.1) which had a tapered sharp edge for cutting easily into the soil (Plate 5.2) with minimal compression of the soil core. A soil core liner (top part of the lysimeter unit) was placed inside the cutting unit, prior to pushing into the soil (Plate 5.3) using the digger. A large block of wood was placed on top of the steel cutting unit (plate 5.4) so the digger bucket could securely and evenly push the cutting unit into the soil to the appropriate depth. A chain was attached to the cutting unit to lift it from the soil with the digger (Plate 5.5). In order to prevent soil falling out of the liner, the soil was removed from around the bottom of the cutting unit (Plate 5.6) so it could be slowly moved onto its side and carefully lifted and sealed. Once the soil filled liner was removed from the cutting unit, it was sealed at both ends with plastic bags and brought to the Johnstown Castle research station for storage.

Plate 5.1 Soil liner (top part of lysimeter unit) inside cutting unit which was used for intact soil core excavation

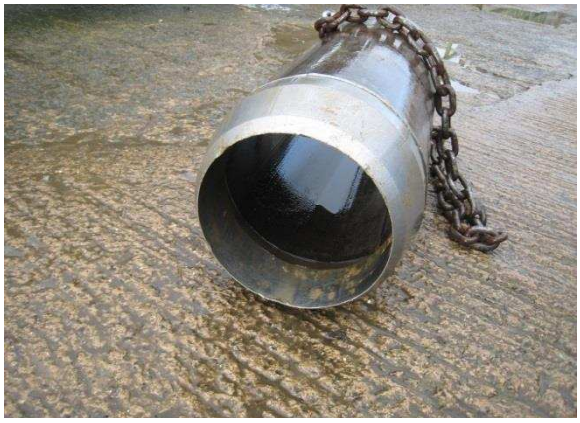


Plate 5.2 Sharp edge on cutting unit to cut easily into soil which was used for lysimeter excavation

Plate 5.3 Entire cutting unit with steel lid on top used for excavating intact soil cores for lysimeters

Plate 5.4 Block of wood placed on top of cutting unit to allow the digger bucket to securely and evenly push the cutting unit into the soil

Plate 5.5 Cutting unit with soil filled liner being lifted from the soil with a digger using a chain

Plate 5.6 Removal of soil from around the bottom of the cutting unit at MT before being lifted and sealed

5.3.5 Lysimeter Setup

Lysimeters were made up of two sections (Figure 5.1). The upper section was the soil filled liner pipe collected in the field. At the time of sampling additional subsoil was collected from the field sites and dried at 40°C and sieved to 4mm. The end of the pipe to be sealed was filled with dried soil to ensure an even and level soil contact was achieved with the bottom plate (plate 5.7). This end of the upper section was then sealed with a plastic plate which had a spout to allow water to drain through. This sealed plate had a fibreglass wick which was glued to the bottom of the plastic plate (plate 5.8). The excess

fibreglass wick was cut off at the edges before sealing. The fibreglass wick was then pushed through the spout and cut to the same length as the spout. This was to allow water to move through the lysimeter and prevent soil blockages in the spout and also to ensure water flowed through the unit under similar tension (created by the fibreglass wick) and didn't sit in the soil until saturation.

Plate 5.7 End of lysimeter pipe filled with dried soil to ensure an even and level soil contact was achieved with the bottom plate

Plate 5.8 Fibreglass wick to allow water to flow through the lysimeter unit under similar tension as soil

Once the plastic plate was welded to the bottom of the upper lysimeter section, the pipe was inverted and then attached to a lower section of the lysimeter unit, the leachate collection sump (figure 5.1), with a rubber coupler to hold the two pipes together. This was then tightened using jubilee clips. A small pipe, 5mm in diameter was inserted into the outer pipe of the lysimeter (figure 5.1). This is the pipe that was used for collecting water. Once this was in position at the bottom of the collection sump it was sealed in place using silicone. Once the lysimeters were complete they were stored at the Johnstown Castle research centre until installation at the field sites.

5.3.6 Lysimeter Installation

Once the lysimeter units were completed they were brought to the field for installation. A Giddings hydraulic soil drilling machine (Giddings machine company, 631 Technology circle, Windsor, CO) was used to drill a 28cm diameter hole (plate 5.9) 1.7 metres deep and the lysimeter unit was then installed into the hole, packed with soil around its perimeter (to prevent preferential flow) and the topsoil was placed over it. The pipe for retrieving drainage water samples (leachate) was buried below the plough layer for ploughing each year and dug up again after ploughing for leachate sampling during the growing season.

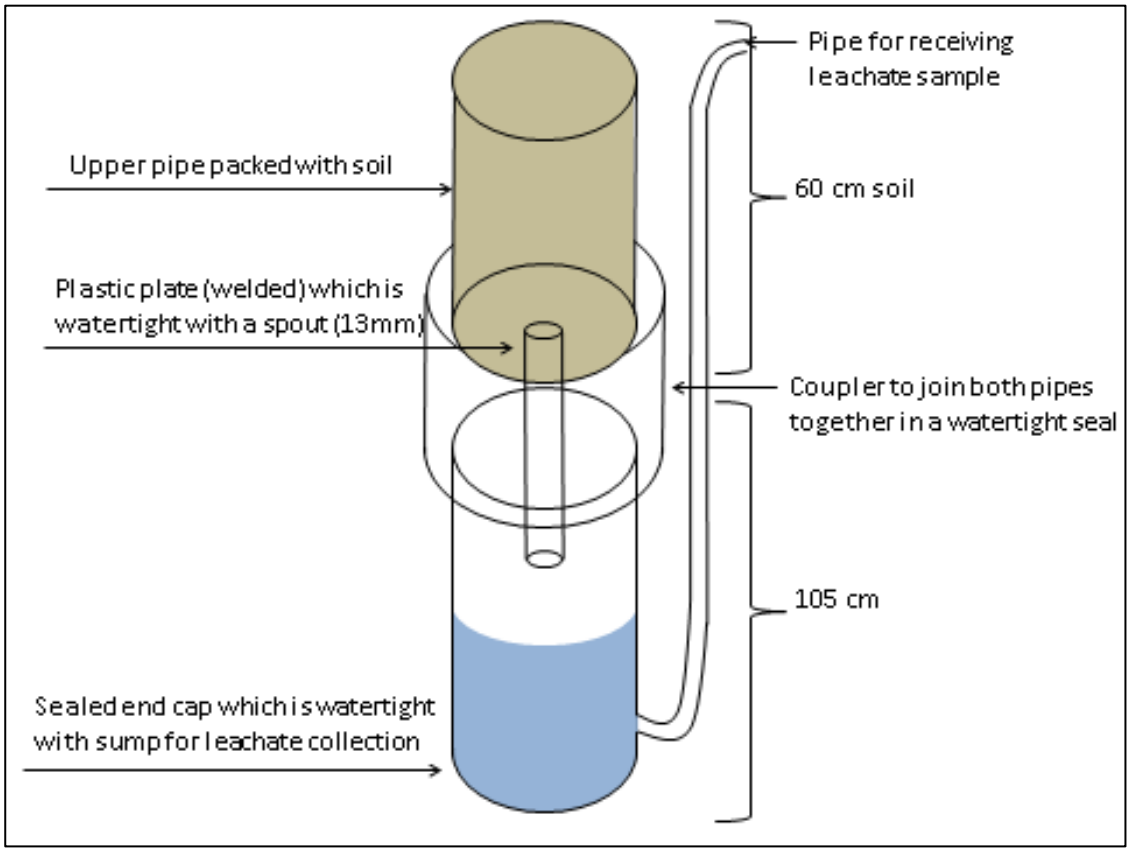


Figure 5.1 Lysimeter setup for measuring NO_3^- leaching

5.3.7 Lysimeter sampling

Leachate sampling was conducted approximately once every three weeks and sometimes more often during periods of high rainfall. Sampling was conducted using a peristaltic pump (Plate 5.10) and the volume of water collected was recorded and a subsample was taken for chemical analysis. Chemical analysis of total oxidised N (TON) and NH_4^+ were determined colorimetrically using an Aquakem 600A (Aquakem 600 A, 01621, Vantaa, Finland). Total oxidised N contains both NO_3^- and NO_2^-, and NO_2^- levels measured were essentially zero and so TON values are called NO_3^- values from here on in. Total N (TN) was analysed using a Shimadzu TOC-TN analyser (Shimadzu Scientific Instruments, USA) via oxidative combustion and chemiluminescence detection (Ammann et al., 2000). Dissolved organic N (DON) was calculated by subtracting inorganic N (TON and NH_4^+) from TN, and was assumed to be the total organic N in the lysimeter drainage water.

Plate 5.9.Giddings hydraulic soil drilling machine for drilling holes for lysimeters.

Plate 5.10 Lysimeter sampling using peristaltic pump

5.3.8 Soil and Climatic Analysis

At both field sites a nearby weather station (located < 1 km from the field sites) (Campbell Scientific BWS-200) was used to determine the climatic conditions during the experiment. These weather stations measured sub-hourly rainfall and standard meteorological parameters (air temperature, relative air humidity, global radiation and wind speed) for estimation of potential evapotranspiration (PET) according to Pennmann-Monteith.

5.3.9 Calculations for N leaching

The drainage water analysis provided the concentration of the various forms of N (mg L^{-1}) collected from each lysimeter on each sampling day. Using a series of calculations, the cumulative annual N leached from each lysimeter was estimated. The quantity of N leached per lysimeter was calculated using the following equation:

$$\textit{Quantity of N leached (mg N lys}^{-1}\textit{) = N concentration (mg N L}^{-1}\textit{) x drainage (L)}$$

Equation 5.1 Calculation for the quantity of N leached from each lysimeter (mg N lys^{-1})

Where the N concentration was for the form of N leached (mg N L^{-1}) from the volume of drainage water (L) collected on the day of sampling. The cumulative N leached in kg ha^{-1} was then calculated using the following equation:

$$\textit{Cumulative N leached (kg ha}^{-1}\textit{) = quantity of N leached (mg N lys}^{-1}\textit{) x } C_{SA} \textit{ x } C_{KG}$$

Equation 5.2 Calculation for cumulative N leached from each lysimeter (kg ha^{-1})

where the cumulative N leached (kg N ha^{-1}) was the total N leached from the lysimeter for the measurement period and the quantity of N leached was from equation 6.1. The C_{SA}

value was the conversion factor for lysimeter surface area to hectares and was 275584, and C_{KG} was the conversion factor for mg to kg and was 0.000001.

5.3.10 Statistical Analysis

Statistical analysis was conducted using the PROC GLIMMIX procedure in SAS 9.3 (2002-2010, SAS Institute Inc., Cary, NC, U.S.A.) on cumulative loads leached (kg ha^{-1}). Significant differences between N fertiliser treatments (and N rates) were determined according to the F-protected least significant difference test ($P<0.05$). The variables included in the model were site year and treatment and the interaction of both were tested as fixed effects and replicate was included as a random effect.

5.4 Results

5.4.1 Results from the Marshalstown site

5.4.1.1 Climatic conditions and drainage

In 2014 the daily air temperature ranged from -2.4°C – 20.1°C with an average of 10.3°C. The highest temperatures occurred during the summer months with the lowest temperatures occurring during the winter months (Figure 5.2). In 2015 the daily air temperature ranged from 0.5°C – 17.7°C with an average of 9.7°C. The highest temperatures for 2015 were also in the summer with the lowest temperatures in the winter months (Figure 5.3). Total rainfall in 2014 was 986 mm with total effective rainfall 619mm and total drainage 795 mm (Figure 5.4). Total rainfall in 2015 was 1174 mm with total effective rainfall 682mm and total drainage was 881mm (Figure 5.4). The highest rainfall occurred in the winter months in both years but there was higher rainfall in the summer months in 2015 compared to 2014.

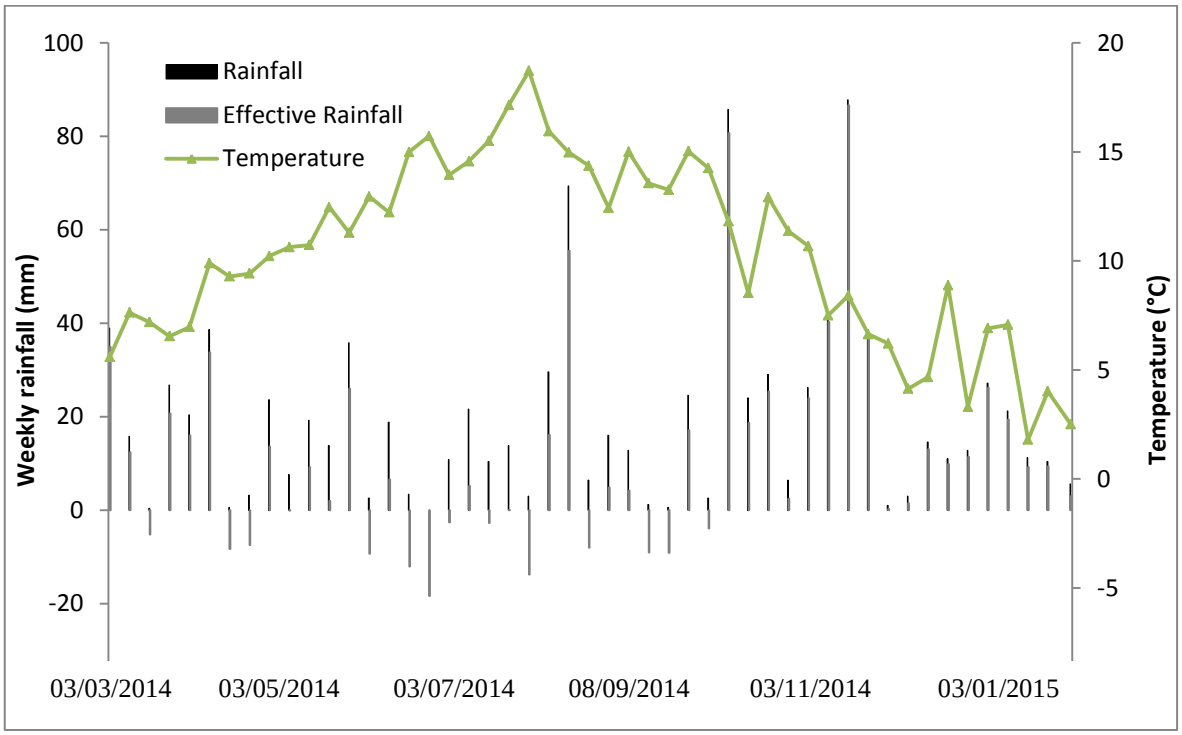


Figure 5.2 Weekly rainfall (mm), effective rainfall (mm) and air temperature (°C) for MT 2014

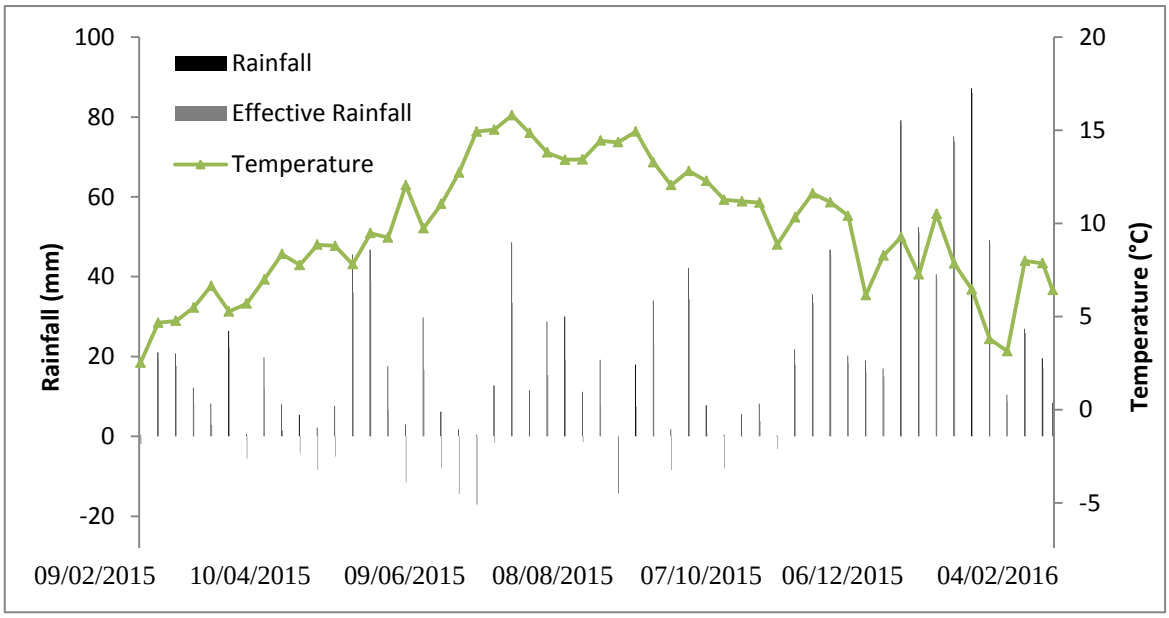


Figure 5.3 Weekly rainfall (mm), effective rainfall (mm) and air temperature (°C) for MT 2015

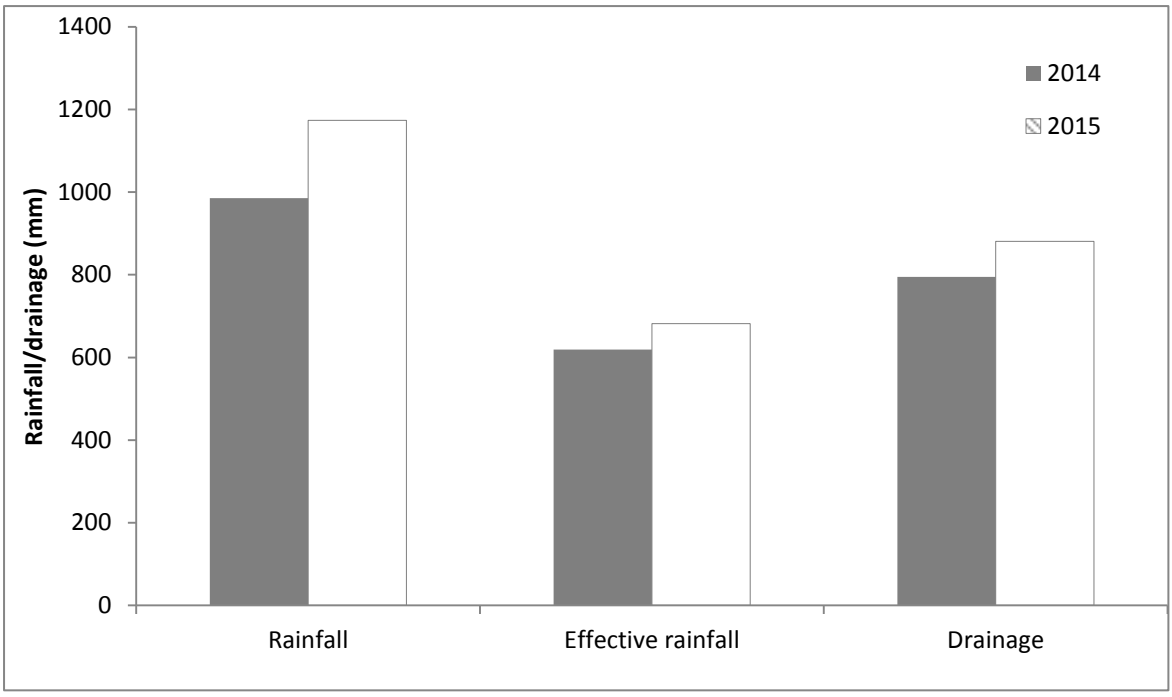


Figure 5.4 Total annual rainfall (mm), effective rainfall (mm) and lysimeter drainage (mm) for MT in both years

5.4.1.2 Temporal NO_3^- concentrations

5.4.1.2.1 CAN at different rates

Peak NO_3^--N concentrations occurred after crop harvest each year with the highest NO_3^- -N concentration from CAN @ 200 kg N ha^{-1} in 2014 of 29.06 mg l^{-1} on 02/10/2014 and from CAN @ 150 kg N ha^{-1} in 2015 of 14.37 mg L^{-1} on 23/11/2015 (Figure 5.5). The average annual NO_3^--N concentration of CAN @ 100 kg N ha^{-1} was 4.83 mg L^{-1} in 2014 and 6.54 mg L^{-1} in 2015. The average annual NO_3^--N concentration for CAN @ 150 kg N ha^{-1} was 8.52 mg L^{-1} in 2014 and 7.26 mg L^{-1} in 2015. The average annual NO_3^--N concentration for CAN @ 200 kg N ha^{-1} was 10.13 mg L^{-1} in 2014 and 6.38 mg L^{-1} in 2015. The average annual NO_3^--N concentration for the unfertilised control was 5.71 mg L^{-1} in 2014 and 6.19 mg L^{-1} in 2015.

5.4.1.2.2 Comparison of N fertiliser formulations

Three N fertiliser formulations were evaluated (CAN, urea and urea + NBPT + DCD) at an N fertiliser rate of 150 kg N ha^{-1}. Peak NO_3^--N concentrations occurred after harvest each year with the highest NO_3^--N concentrations in 2014 from CAN of 23.66 mg l^{-1} on 21/10/2014 and the highest NO_3^--N concentration in 2015 from Urea + NBPT + DCD of 15.84 mg l^{-1} on 08/12/2014 (Figure 5.6). The average annual NO_3^--N concentration for CAN was 8.52 mg L^{-1} in 2014 and 7.26 mg L^{-1} in 2015. The average annual NO_3^--N concentration for urea was 9.61 mg L^{-1} in 2014 and 8.36 mg L^{-1} in 2015. The average annual NO_3^--N concentration for Urea + NBPT + DCD was 11.98 mg L^{-1} in 2014 and 9.82 mg L^{-1} in 2015. The average annual NO_3^--N concentration for the control was 5.71 mg L^{-1} in 2014 and 6.19 mg L^{-1} in 2015.

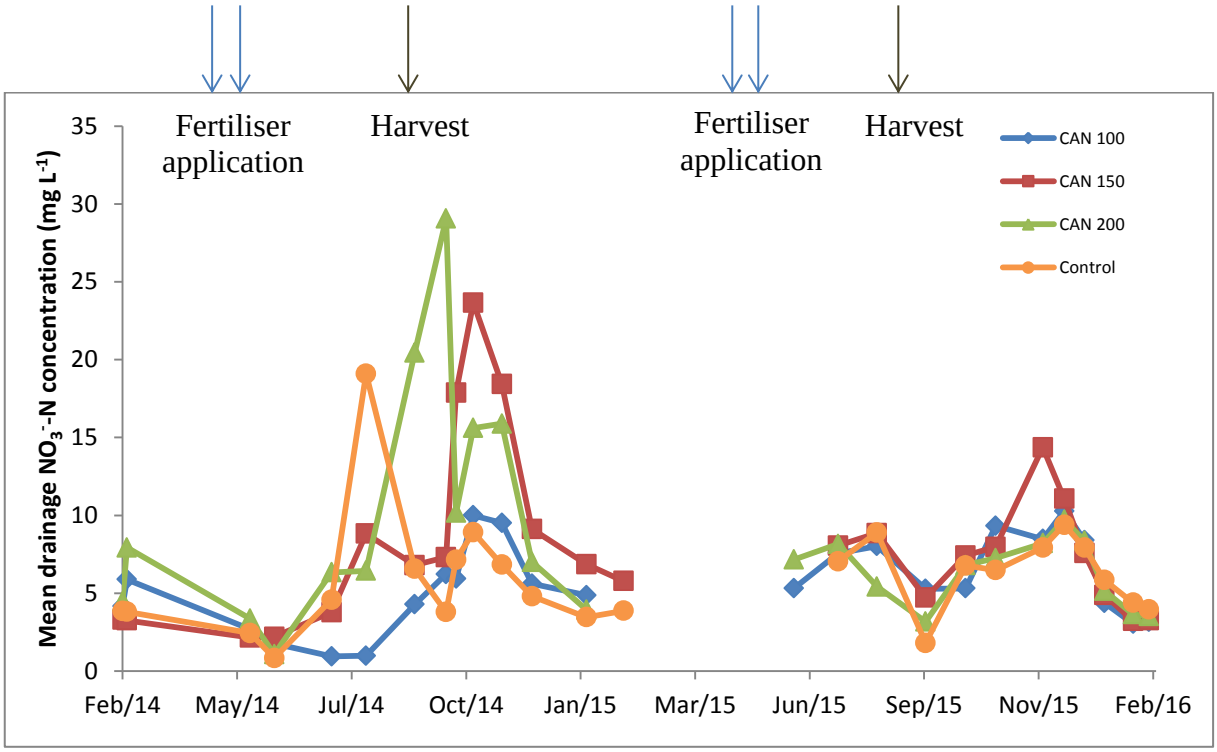


Figure 5.5 Temporal NO_3^--N concentrations for CAN at different rates from February 2014 – February 2016

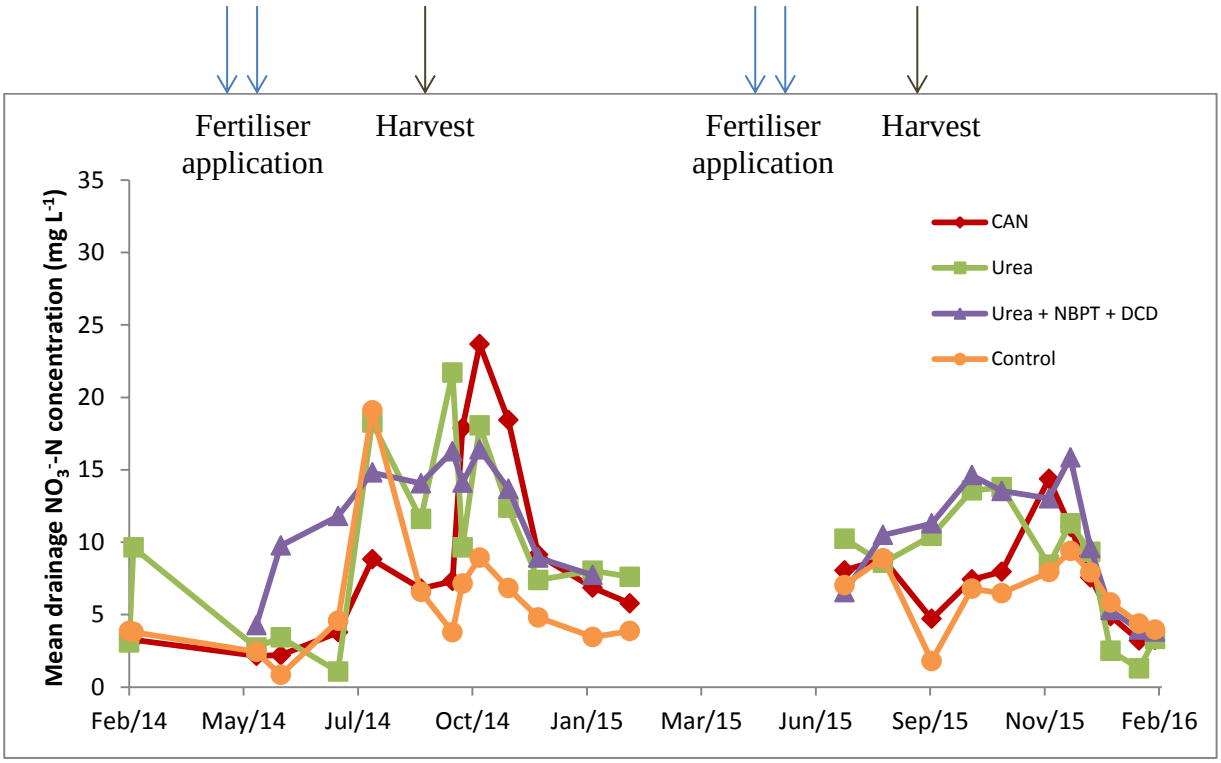


Figure 5.6 Temporal NO_3^--N concentrations for comparison of N fertiliser formulations from February 2014 – February 2016

5.4.1.3 Cumulative leaching losses

5.4.1.3.1 Effect of fertiliser nitrogen rate at different rates of CAN on leachate

5.4.1.3.1.1 NO_3^--N

There was no interaction of year x rate for cumulative NO_3^--N losses ($P>0.05$) (Table 5.1) but there was an N fertiliser rate effect ($P<0.05$). CAN @150 kg N ha^{-1} had the highest NO_3^--N leaching losses of 62.76 kg N ha^{-1} and was significantly higher than CAN @ 100 kg N ha^{-1} and the unfertilised control but not significantly different to CAN @ 200 kg N ha^{-1}(Table 5.3). CAN @ 200 kg N ha^{-1} had NO_3^--N leaching losses of 41.21 kg N ha^{-1} which was not significantly different to any other rate. The mean NO_3^--N leaching for CAN @ 100 kg N ha^{-1} was 29.98 kg N ha^{-1} which was not significantly different to the unfertilised control with 36.69 kg N ha^{-1} or CAN @ 200 kg N ha^{-1}.

5.4.1.3.1.2 NH_4^+-N

There was a significant interaction of year x rate for cumulative NH_4^+-N losses ($P<0.05$) (Table 5.1). The unfertilised control in 2014 represented the highest cumulative NH_4^+-N loss of 1.26 kg N ha^{-1} which was not significantly different than losses from CAN @ 200 kg N ha^{-1} of 1.02 kg N ha^{-1}. Both of these treatments were significantly higher than all other treatments and the cumulative NH_4^+-N loss for all other treatments were not different from each other.

5.4.1.3.1.3 DON

There was no interaction of year x rate for cumulative DON losses ($P>0.05$) (Table 1.1) and there was also no significant rate effect but there was a significant year effect ($P<0.05$). The cumulative DON losses for 2014 were 3.15 N ha^{-1} which was significantly lower than in 2015 where the cumulative DON loss was 12.01 kg N ha^{-1}(Table 5.2)

5.4.1.3.1.4 TN

There was no significant interaction of year x rate for TN losses ($P>0.05$ (Table 5.1) and there was also no significant rate or year effect ($P>0.05$). The cumulative TN loss was 49.51 kg N ha^{-1}.

5.4.1.3.2 Effect of N fertiliser formulation (applied at a rate of 150 kg N ha^{-1}) on leachate

5.4.1.3.2.1 NO_3^--N

There was no interaction of year x N fertiliser formulation for cumulative NO_3^--N losses ($P>0.05$) and there was also no significant rate or year effect ($P>0.05$) (Table 5.4). The cumulative NO_3^--N loss was 50.81 kg N ha^{-1}.

5.4.1.3.2.2 NH_4^+-N

There was a significant interaction of year x N fertiliser formulation for cumulative NH_4^+-N loss ($P<0.05$) (Table 5.4). The unfertilised control in 2014 had the highest NH_4^+-N loss of 1.29 kg N ha^{-1} which was significantly higher than all other treatments. All other treatments were not significantly different from each other.

5.4.1.3.2.3 DON

There was no interaction of year x N fertiliser formulation for cumulative DON losses ($P>0.05$) (Table 5.4) and there was also no significant N fertiliser formulation effect but there was a significant year effect ($P<0.05$). The cumulative DON loss for 2014 was 3.74 kg N ha^{-1} which was significantly lower than in 2015 which was 13.70 kg N ha^{-1} (Table 5.5).

5.4.1.3.2.4 TN

There was no significant interaction of year x N fertiliser formulation on cumulative TN losses ($P>0.05$) (Table 5.4) and there was also no significant N fertiliser formulation or year effect ($P>0.05$). The cumulative TN loss was 58.40 kg N ha^{-1}.

Table 5.1 Significant effects and mean NO_3^--N, TN, DON and NH_4^+-N loads leached (kg ha^{-1}) as affected by CAN fertiliser rates in 2014 and 2015

Effect		**NO_3^--N**	**TN**	**DON**	**NH_4^+-N**
Year		ns	ns	*	**
Rate		*	ns	ns	*
Year*Rate		ns	ns	ns	*
Year	**N rate**	**TON**	**TN**	**DON**	**NH4**
	(kg N ha^{-1})		**(kg N ha^{-1})**		
2014	100	21.04	23.11	2.44	0.07b
2014	150	65.85	69.15	4.79	0.11b
2014	200	43.05	45.69	2.31	1.02a
2014	Control	34.37	32.82	3.05	1.26a
2015	100	38.92	50.10	11.13	0.03b
2015	150	59.66	75.68	15.93	0.08b
2015	200	39.38	50.39	10.94	0.07b
2015	Control	39.00	49.13	10.03	0.10b
Average			**49.51**		

*Different letters represent significant differences between N rates using F protected LSD test (P<0.05)
*ns = not significant, * = P<0.05, ** = P<0.01

Table 5.2 Effect of year on the mean DON loads leached (kg N ha^{-1})

Year	**DON (kg N ha^{-1})**
2014	3.15b
2015	12.01a

*Different letters represent significant differences between N rates using F protected LSD test (P<0.05)

Table 5.3 Effect of N rate on the mean NO_3^--N loads leached (kg N ha^{-1})

N Rate	TON (kg N ha^{-1})
0	36.69b
100	29.98b
150	62.76a
200	41.21ab

*Different letters represent significant differences between N rates using F protected LSD test (P<0.05)

Table 5.4 Significant effects and mean NO_3^--N, TN, DON and NH_4^+-N loads leached (kg N ha^{-1}) as affected by N fertiliser source

Effect		TON	TN	DON	NH4
Year		ns	ns	**	***
Treatment		ns	ns	ns	***
Year*Treatment		ns	ns	ns	***
Year	**Treatment**	**TON**	**TN**	**DON**	**NH4**
			Kg N ha^{-1}		
2014	CAN	65.85	69.15	4.79	0.11b
2014	Urea	49.52	49.24	2.47	0.23b
2014	UAD*	53.07	57.13	4.63	0.12b
2014	Control	34.37	32.82	3.06	1.29a
2015	CAN	59.66	75.68	15.93	0.08b
2015	Urea	40.55	51.85	2.47	0.16b
2015	UAD	64.43	82.24	17.71	0.11b
2015	Control	39.00	49.13	10.03	0.10b
Average		**50.81**	**58.40**		

*UAD is urea + NBPT + DCD
*Different letters represent significant differences between N fertiliser formulations using F protected LSD test (P<0.05)
*ns = not significant, ** = P<0.01, *** = P<0.001

Table 5.5 Effect of year on the mean DON loads leached (kg N ha^{-1})

Year	DON
2014	3.74b
2015	13.70a

*Different letters represent significant differences between years using F protected LSD test ($P<0.05$)

5.4.2 Johnstown Results

5.4.2.1 Drainage

The total rainfall for Johnstown in 2014 was 9356 mm and effective rainfall was 533 mm. Effective rainfall is also known as effective drainage and it would be expected that the drainage through the lysimeters would be somewhat similar to the effective rainfall. This was not the case in Johnstown. In 2014, fourteen of the lysimeters had more than the double the quantity of effective rainfall with the highest quantity from lysimeter 18 of 2680mm drainage (Figure 5.7). Five of the lysimeters had less than half the effective rainfall and only five of the lysimeters gave realistic drainage volumes which ranged from 316mm – 794mm.

The total rainfall for Johnstown in 2015 was 1032.5mm and effective rainfall was 615mm. Fifteen of the lysimeters in 2015 were more than double the effective rainfall with the highest quantity from lysimeter 20 with 5115mm drainage (Figure 5.8). Four of the lysimeters had high drainage volumes that were close to double the effective rainfall ranging from 1012mm – 1197mm. Only three of the lysimeters in 2015 had realistic drainage volume which ranged from 328mm – 728mm.

These high and variable drainage volumes can be explained by the water table depth during the winter and early spring period at this moderately drained JC site. The top of the lysimeters were buried 30cm below the soil surface on this arable site (to facilitate cultivation etc.). Measurement of depth to groundwater at this site indicated that the shallow groundwater rose above the top of the lysimeters during the winter and early spring. This increased the drainage volume entering the lysimeters explaining the high drainage volumes recorded. Therefore the N species concentration in the drainage water also included that of the shallow groundwater which means treatment effects could not be assessed at this site. As the drainage water volume is used to calculate the N load leached

(kg ha^{-1}) this overestimated the TON loads lost and so leaching results for Johnstown are not shown.

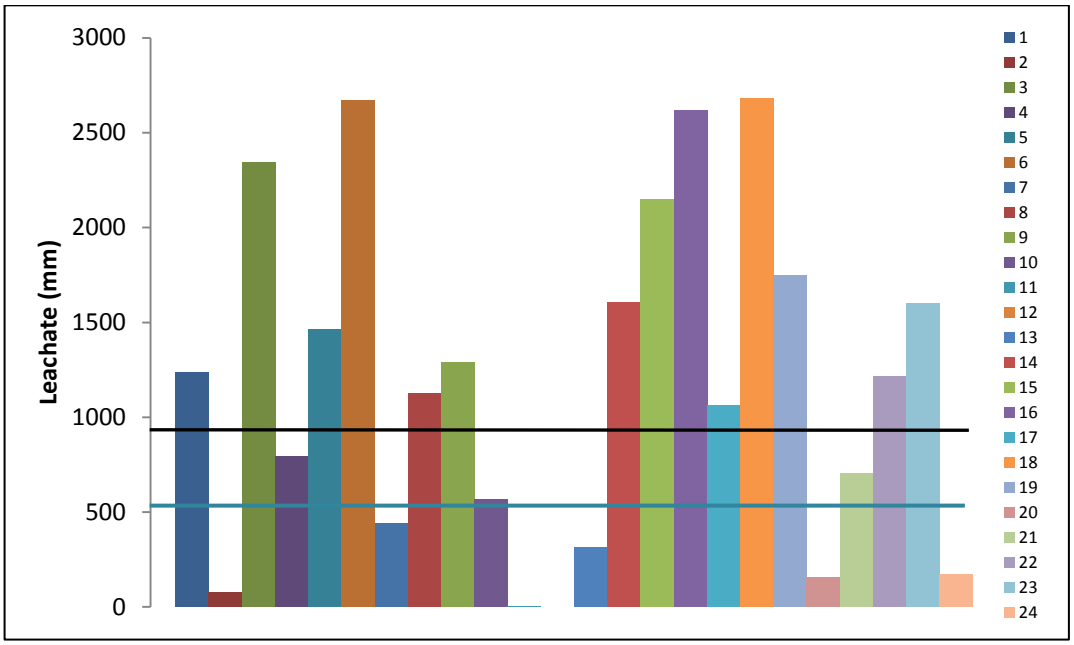


Figure 5.7 Annual drainage volumes (mm) from each lysimeter (1-24) at JC in 2014

*The black line represents total annual rainfall (mm) and the blue line represents total annual effective rainfall (mm)

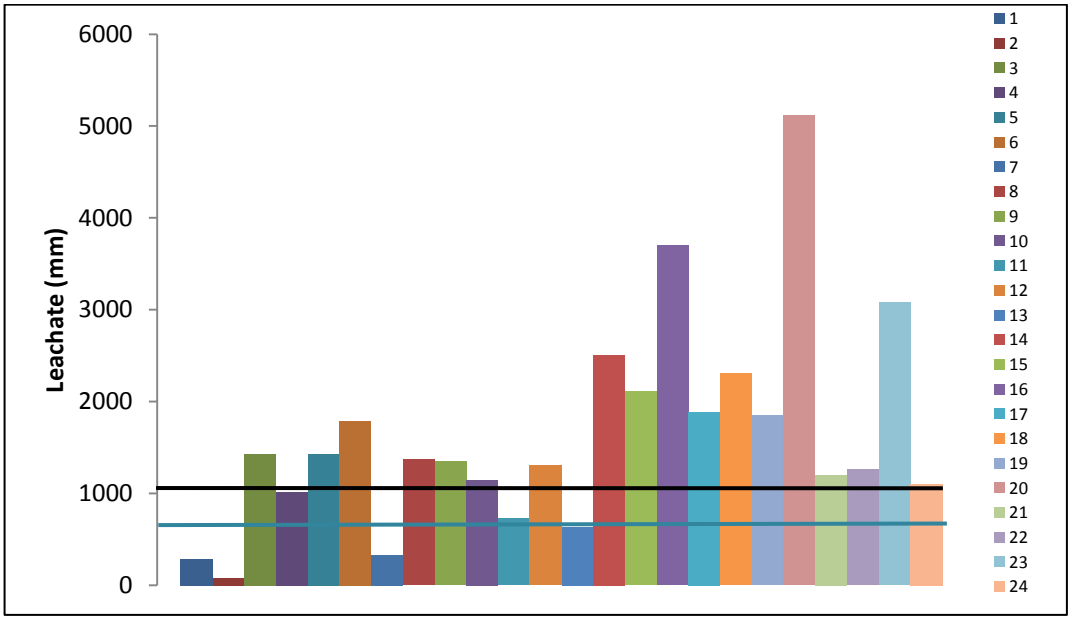


Figure 5.8 Annual drainage volumes (mm) from each lysimeter (1-24) at JC in 2015

*The black line represents total annual rainfall (mm) and the blue line represents total annual effective rainfall (mm)

5.5 Discussion

5.5.1 Effect of N fertiliser formulation on mean NO_3^--N concentrations

The fertiliser formulations evaluated were CAN, urea and urea + NBPT + DCD and were all applied at the rate of 150 kg N ha^{-1}. The highest NO_3^--N concentration observed in leachate water was 23.66 mg N L^{-1} from CAN which occurred in October, during the fallow period after the crop was harvested. In general, for all N fertiliser formulations, this was the time of year with the highest NO_3^--N concentrations. Other studies have also shown highest NO_3^--N leaching at this time of the year in arable cropped soils (Shepherd and Lord, 1996; Goulding, 2000; Pappa et al., 2011). In this current study, the highest NO_3^--N concentrations from individual sampling periods were approximately double the drinking water limit of 11.3 mg N L^{-1}. On average over the annual measurement period the only formulation with leachate NO_3^--N concentrations above the drinking water limit was urea + NBPT + DCD with 11.98 mg NO_3^--N L^{-1}. Studies on cover crops (catch crops) sown after cereal harvest can reduce NO_3^- leaching concentrations (Hooker et al., 2008; Premrov et al., 2014). Premrov et al. (2014) showed that mean NO_3^--N concentrations where no cover crop was planted (i.e. natural regeneration of vegetation over the winter period) were 13.9 mg N L^{-1} and where a mustard cover crop was sown, it reduced the mean NO_3^--N concentrations to 3.3 mg N L^{-1}.

5.5.2 Effect of N fertiliser rate on mean NO_3^--N concentrations

The N fertiliser rates evaluated were CAN @ 100, 150 and 200 kg N ha^{-1}. The highest NO_3^--N concentration observed in leachate water was 29.061 mg N L^{-1} from CAN @ 200 kg N ha^{-1} which occurred in October which was during the fallow period after the crop was harvested. Similar to section 5.5.1 comparing N fertiliser formulations this was the time of

the year with the highest NO_3^--N concentrations. Sowing cover crops after harvest can reduce NO_3^--N leaching concentrations which are discussed in more detail in section 5.5.1.

5.5.3 Effect of N fertiliser formulation on NO_3^--N loads leached (kg N ha^{-1})

There was no effect of N fertiliser formulation on cumulative NO_3^--N loads leached. The NO_3^--N losses ranged from 34.37 kg N ha^{-1} to 65.85 kg N ha^{-1} across the N fertiliser formulations applied at a rate of 150 kg N ha^{-1} applied. This is in agreement with other studies within this catchment. McAleer et al. (2016) found leaching losses of 67.33 kg N ha^{-1} in 2012 with N input of 137 kg N ha^{-1} and 57.56 kg N ha^{-1} in 2013 with N input of 150 kg N ha^{-1}. Melland et al. (2012) measured TON at stream outlets at the same catchment and found 35 kg ha^{-1} in 2010 and 22 kg ha^{-1} in 2011. These stream N loads were lower compared to those found in the current leachate study, however, this would be expected as natural N attenuation processes are likely to occur at the river catchment scale reducing the N load in groundwater and streamwater. Premrov et al. (2014) observed leaching losses of between approximately 30 kg N ha^{-1} – 105.7 kg N ha^{-1} from spring barley on a well-drained sandy soil in Ireland. Overall, NO_3^--N leaching losses found in this study are comparable to losses found in other studies.

Previous studies have observed that the greatest proportion of N leached originates from mineralisation of background soil N (Gioacchini et al., 2002; Cameron et al., 2013). Peak NO_3^--N concentrations occurred after harvest which is a time when the land is fallow and any NO_3^--N present in the soil is more easily lost as there is no plant N uptake. Other studies have also shown highest NO_3^- leaching at this time of the year in arable cropped soils (Shepherd and Lord, 1996; Goulding, 2000; Pappa et al., 2011).

Studies have shown that sowing cover crops after harvest can reduce NO_3^--N leaching. Premrov et al. (2014) showed that mustard cover crop significantly reduced mean NO_3^- concentrations compared to natural regeneration (NR) and no cover (NC) by more than 70% (average reduced loads of 19.4 – 52.3 kg ha^{-1}) on a similar free-draining soil type cropped with spring barley. Natural regeneration (NR) also reduced NO_3^- concentrations by 42% compared to no cover (NC). Hooker et al. (2008) also showed NO_3^- concentration reductions using mustard cover crop on the same site. Other cover crop studies on a similar climate also showed reductions compared to NR and NC (Shepherd, 1999; Shepherd and Webb, 1999; Macdonald et al., 2005; Feaga et al., 2010). Overall, NO_3^- leaching losses were similar regardless of the fertiliser N source used and results from other studies indicate that using a cover crop in the winter period is a good method to reduce NO_3^- leaching.

Nitrate leaching contributes to indirect losses of N_2O contributing to national GHG emissions and is calculated in the GHG inventory using a default EF of 0.015% (Nevison, 2002). There was no significant effect of N fertiliser formulation in this study on NO_3^- leaching and consequently N fertiliser formulation will have little effect on the calculation of indirect emissions of N_2O from leached NO_3^-. This study indicates that similar emission factors should be applied to CAN, urea and urea + NBPT + DCD for indirect N_2O emissions from leached NO_3^-.

5.5.4 Effect of N fertiliser formulation on other N leaching losses (kg N ha^{-1})

There was no effect of year or treatment on TN losses but there was a significant interaction of year x treatment on NH_4^+ leaching losses and there was a significant year effect on DON leaching losses.

The quantity of NH_4^+ leaching losses was small ranging from 0.08 kg ha^{-1} to 1.29 kg ha^{-1}. The unfertilised control had the highest losses of 1.29 kg NH_4^+-N ha^{-1}. This was higher than all other fertiliser formulations which were not different to each other. As shown in chapter 8, the crop yields and N uptake from the unfertilised control plots were significantly lower than the fertilised plots showing there was lower plant N uptake and therefore higher potential for leaching of mineralised N from unfertilised control plots. Overall the quantity of NH_4^+-N leached from the different N fertiliser formulations was less than 1% of the N applied and so is negligible compared to TON and DON losses. Previous studies have also shown NH_4^+-N leaching losses to be negligible ((Brown et al., 1982; Mancino and Troll, 1990).

DON losses in 2014 were 3.74 kg N ha^{-1} which was significantly lower than 2015 where DON losses were 13.70 kg N ha^{-1}. DON losses from agricultural systems can vary and Van Kessel et al. (2009) reviewed 16 studies to show that these losses vary between 0.3 kg DON ha^{-1} $year^{-1}$ in grass clover systems to 127 kg DON ha^{-1} $year^{-1}$ in a pasture following urine application with a mean value average across all experimental sites and treatments of 12.7 kg N ha^{-1}. Leaching of DON can have negative environmental impacts the same as NO_3^-, causing eutrophication and acidification and can also pose a potential risk to human health (Van Kessel et al., 2009). The losses in the current study are comparable to this mean loss value reported in Van Kessel et al. (2009). Dissolved organic N losses are expected to be lower than NO_3^--N losses as NO_3^- is highly soluble and not bound by clay minerals (Feigenbaum et al., 1994). Switching N fertiliser source did not have an effect on DON loss levels.

The main sources of DON losses in agricultural systems are from crop residues and soil organic matter, with DON being formed as part of the decomposition process (Van Kessel

et al., 2009). The difference in DON losses between the two years could be down to differences in weather and levels of N mineralisation.

Overall, in terms of the different N species measured in leachate, NO_3^--N and DON losses were of more importance agronomically and environmentally, as up to 13.70 kg N ha^{-1} was lost as DON and up to 65.85 kg N ha^{-1} was lost as NO_{3-}-N.

5.5.5 Effect of N fertiliser rate on nitrate loads leached (kg N ha^{-1})

There was a significant effect of N rate on NO_3^--N leached with the highest NO_3^--N leached from CAN @ 150 kg N ha^{-1} and CAN @ 200 kg N ha^{-1} in 2014 and 2015. Overall, where the application rates of CAN > 150 kg N ha^{-1} , they had higher NO_3^--N leached than CAN @ 100 kg N ha^{-1} and the unfertilised control. However, the unfertilised control, CAN @ 100 kg N ha^{-1} and CAN @ 200 kg N ha^{-1} were not statistically different from each other. CAN @ 150 and 200 kg N ha^{-1} had the highest N losses in the current study which is in agreement with other studies showing higher losses of NO_3^--N with higher rates of N fertiliser applied (Goulding, 2000; Di and Cameron, 2002b).

5.5.6 Effect of N fertiliser rate on other N leaching losses (kg N ha^{-1})

There was no effect of N rate or year on TN leaching losses but there was a significant effect of year x treatment on NH_4^+ losses and there was a significant year effect on DON losses.

The highest NH_4^+ losses were from the unfertilised control and CAN @ 200 kg N ha^{-1} in 2014 with the highest losses of 1.26 kg N ha^{-1} and 1.02 kg N ha^{-1} respectively. These losses are negligible from both agronomic and environmental perspectives and they are less than 1% of the N applied across the fertilised treatments.

In 2014 DON losses were 3.15 kg N ha^{-1} which was significantly lower than 12.01 kg N ha^{-1} in 2015. As explained above in section 5.5.3.1, DON leaching losses can contribute substantially to overall N leaching losses and should be considered when evaluating N losses at river catchment or regional scales There was no effect of N rate on DON losses. The main sources of DON losses in agricultural systems are crop residues and soil organic matter, with DON usually resulting from decomposition processes (Van Kessel et al., 2009). In this study DON is resulting from SOM decomposition processes and the difference between the two years can be attributed to differences in N mineralisation rates affected by weather. Temperatures were similar in both years but there was higher rainfall in 2015 which occurred in the winter months with mild temperatures therefore promoting higher N mineralisation than in 2014.

5.6 Conclusions

There was no effect of N fertiliser formulation on NO_3^- or DON leaching losses and so, switching N fertiliser formulation will not effectively reduce leached N losses in long term arable soils. The NO_3^--N leaching losses measured in this study were comparable with other studies on spring barley systems and may have implications for indirect N_2O emissions.

Nitrate-N concentrations in leachate from arable soils used for spring barley production were above the drinking water limit, periodically, for all N fertiliser sources. Therefore, management of arable land used for spring barley is required to mitigate these losses to minimise adverse effects to water bodies used as drinking water sources. Studies have shown that the establishment of cover crops post cereal crop harvest can reduce NO_3^--N leaching losses to below the drinking water limit of 11.3 mg N L^{-1}. Further research is

needed on the management of cover crops in the fallow period for spring barley to establish the environmental and agronomic benefits over longer durations.

The results from this study reject the hypothesis that switching N fertiliser formulation will reduce NO_3^- leaching losses. Although NO_3^--N leaching losses were not reduced by using urea + N stabilisers, they did not increase either. However, these studies indicate that N fertiliser formulation effects fNUE by the crop (Chapter 8) which affects the residual N remaining in the soil, available for leaching and other N loss pathways. Further research studies on the effect of each individual N stabiliser (NBPT and DCD) on NO_3^--N leaching losses is required to evaluate their effects over longer durations. Overall, switching N fertiliser formulation to reduce N_2O emissions will not negatively impact NO_3^- leaching.

Chapter 6 - Effect of N fertiliser formulation on ammonia concentrations in spring barley: CAN versus urea and urea + NBPT

6.1 Summary

Agriculture in Ireland accounts for 99% of national NH_3 emissions and the application of urea to soils contributes to these emissions. Under the National Emission Ceilings Directive Ireland must reduce NH_3 emissions by 5% below 2005 levels by 2030. Switching N fertiliser source from CAN to urea based formulations can potentially reduce N_2O emissions (discussed in chapter 4) but could potentially increase N loss through NH_3 emissions due to the ammonia volatilisation process. Urease inhibitors have been shown to reduce NH_3 emissions but there is limited information on NH_3 emissions from urease inhibitors in Ireland, with no study investigating emissions from spring barley. The objective of this study was to assess the effect of CAN and urea on NH_3 concentrations and to assess the effect of the urease inhibitor NBPT at reducing NH_3 concentrations compared to urea with a hypothesis that using urea stabilised with the urease inhibitor NBPT will reduce NH_3 losses compared to urea. Ammonia concentrations were measured using passive shuttles and results are presented as a relative comparison of NH_3 concentrations (mg L^{-1}) for the N fertiliser formations tested, as the NH_3 concentrations were not quantified (i.e. not expressed on a kg ha^{-1} basis). Results show that urea had the highest relative NH_3 concentrations for the measurement period which were significantly higher than CAN and urea + NBPT. Ammonia concentrations from CAN and urea + NBPT were not different from one another. Overall this study shows that using urea stabilised with the urease inhibitor NBPT can protect against NH_3 loss potential when using urea. However, this was a preliminary study showing relative differences and further research using quantitative methods is required.

6.2 Introduction:

In 2008 global NH_3 emissions had increased to approximately 65.4 Tg N yr^{-1} (Sutton et al., 2013). Approximately 60% of atmospheric NH_3 emissions arise from anthropogenic sources (Asman et al., 1998) and 94% of global emissions and 99% of Irelands emissions came from agriculture (FAOSTAT, 2013; EPA, 2015). Beusen et al. (2008) estimated annual NH_3 emissions from fertiliser N to be between 10 and 12 Tg N yr^{-1}.

Ammonia emissions lost to the atmosphere are redeposited on land and water surfaces causing eutrophication and acidification of natural ecosystems (Sommer and Hutchings, 2001). This redeposited NH_3 can also contribute to indirect losses of N_2O. As a result, a number of EU countries, including Ireland are committed to reducing NH_3 emissions under the National Emission Ceilings (NEC) directive and the Gothenburg Protocol. The Gothenburg Protocol which aims to abate acidification, eutrophication and ground-level ozone was established in 1999 by the United Nations Economic Commission for Europe (UNECE). In addition, the EU National Emission Ceilings (NEC) Directive implements the Gothenburg Protocol targets (EU, 2001), with changes proposed to the NEC requiring NH_3 reduction targets of 5% below 2005 levels by 2030 (EC, 2013). In contrast, models of production increases under Food Wise 2025 project that primary production will increase by 65%. An increase in synthetic N fertiliser is essential to achieve these targets and this could potentially result in an increase in NH_3 emissions.

Globally urea is the dominant source of synthetic N fertiliser accounting for approximately 50% of the total N fertiliser consumption in the world (Sanz-Cobena et al., 2008). The dominant N fertiliser used in Ireland is calcium ammonium nitrate (CAN). CAN contains 27% N of which 50% is the ammonium form and 50% is in the nitrate form and so immediately contributes to the soil nitrate pool. Nitrate is then available for nitrous oxide (N_2O) losses through denitrification processes. Nitrous oxide is a potent greenhouse gas

(GHG) that contributes to global warming and is the single most important ozone-depleting gas (Ravishankara et al., 2009). Switching from CAN to urea as an alternative N fertiliser formulation has the potential to reduce NH_3 emissions (Chambers and Damney, 2009; Forrestal et al., 2015). However, CAN has been found to have higher direct N_2O emissions than urea as urea is not immediately available for denitrification after application (Dobbie and Smith, 2003a; Harty et al., 2016a).

Abatement strategies for reducing NH_3 emissions from the agriculture sector are necessary. Incorporating the fertiliser into the soil which favours rapid adsorption of NH_4^+ from solution onto soil colloids is one method (Sommer et al., 2004). In arable systems in Ireland the first split fertiliser application is generally incorporated into the soil but subsequent fertiliser applications are surface broadcast and incorporation would not be possible. Using urease inhibitors is another possible way to reduce NH_3 emissions from urea fertiliser especially where urea is surface broadcast (Xiaobin et al., 1995; Grant et al., 1996; Grant and Bailey, 1999; Forrestal et al., 2015). Urease inhibitors work by inhibiting the soil enzyme urease and slowing down urea hydrolysis. This allows more time for urea to diffuse into the soil and reduces the concentration of NH_4^+ in soil solution and potentially reducing NH_3 emissions (Grant et al., 1996).

The most effective urease inhibitors are the thiophosphorotriamides which are structural analogues of urea and effectively block the active site on the soil enzyme urease (Watson et al., 2009). The most commonly used thiophosphorotriamide is N-(n-butyl) thiophosphoric triamide (NBPT) (Watson et al., 2009). Studies have shown that the addition of NBPT to urea is effective at reducing NH_3 emissions compared to urea (Trenkel, 1997; Watson, 2005; Forrestal et al., 2015) and some studies have shown the addition of NBPT to urea to increase crop yields (Grant and Bailey, 1999). The addition of

NBPT to urea has potential to be cost effective and have environmental benefits compared to using CAN (Watson, 2005). However, its effectiveness in spring barley under moist maritime climatic conditions in Ireland has yet to be tested.

The urease inhibitor evaluated in this study was N-(n-butyl) thiophosphoric triamide (NBPT (and also referred to as n-BTPT in other studies)). There is limited information on the effect of urea + NBPT on NH_3 emissions in Ireland. Studies have been conducted on the effect of urea + NBPT at reducing NH_3 losses in grasslands (Watson et al., 1994; Forrestal et al., 2015) and have shown urea + NBPT to reduce NH_3 losses compared to urea. There have been no studies conducted on urea + NBPT on spring barley in Ireland and this study is a preliminary study to assess the effect of urea + NBPT on NH_3 concentrations. The aim of this study was to evaluate the relative differences of NH_3 concentrations from different N fertiliser formulations including CAN and urea with and without the urease inhibitor NBPT. The hypothesis tested was: using urea + NBPT reduces NH_3 concentrations compared to urea in spring barley and produce similar NH_3 concentrations as CAN.

6.3 Materials and Methods

6.3.1 Site description

Field experiments were conducted on a free-draining loam soil located in Marshalstown (MT), Co. Wexford and a moderately draining sandy loam soil located in Johnstown Castle (JC), in Co. Wexford. The sites locations and soil characteristics can be seen in Table 3.1 in chapter 3 and are based on the top 10cm of soil. The MT site had been in long term arable production for approximately 20 years with continuous spring barley production since 2007. The JC site had been in arable production for six years and prior to this it was permanent grassland until 2010 when it was cropped with maize for three years before spring barley. This site received organic manure annually while it was in grassland and maize. The last application of manure was in 2012, 18 months prior to commencing these experiments which started in spring 2014.

6.3.2 Crop husbandry

The spring barley (*Hordeum vulgare* L.) cultivar used was 'Sebastian'. The site was ploughed (20 - 30cm depth) in March 2014 and 2015. The crop was sown in mid-April in both years and was harvested in mid-August in both years. The experiment ran for approximately three weeks in each year (2014 and 2015), after the second split fertiliser application, and daily integrated NH_3 concentrations and cumulative NH_3 concentrations (mg L^{-1}) were generated. The site characteristics are described in Table 3.1 in chapter 3 and are based on the top 10 cm of soil which is the standard agronomic soil sampling depth in Ireland. Each year basal phosphorus (P), potassium (K) and sulphur (S) were applied to the soil, according to the Teagasc Green Book of nutrient advice (Coulter and Lalor, 2008) to prevent nutrient deficiencies from occurring. A robust pesticide programme was applied

to the crop to control weeds, pests and diseases as per standard agronomic practice for spring barley crops (Teagasc, 2016b).

6.3.3 Experimental Design

The experiment consisted of three fertiliser formulations all applied at 150 kg N ha^{-1} which included CAN, urea and urea + NBPT and also a background where no fertiliser was applied. 30 kg N ha^{-1} was applied at sowing which was surface broadcast for this experiment. Generally, in spring barley production systems in Ireland, the 1st split N fertiliser application is incorporated and so there would be minimal NH_3 losses. For this study NH_3 concentrations were not measured from the 1st split fertiliser application for this reason. The second split fertiliser application consisted of 120 kg N ha^{-1} which was surface broadcast and NH_3 concentrations were measured for 20 days and 19 days for 2014 and 2015 respectively after fertiliser application. Ammonia shuttles were installed on masts 0.6m high in the centre of a 10m fertilised circle which is discussed in more detail in section 6.3.3.2. There were two replicates of each treatment at each site year. For statistical analysis of cumulative NH_3 concentrations, each replicate within each site year was considered an individual replicate to give a total of six replicates across the study (Table 6.1).

Table 6.1 Explanation of replicates used for statistical analysis for NH_3 concentration data

Replicates within site year	Individual replicates
JC 2014 rep 1	1
JC 2014 rep 2	2
MT 2014 rep 1	3
MT 2014 rep 2	4
MT 2015 rep 1	5
MT 2015 rep 2	6

6.3.4 Ammonia measurements

Ammonia concentration measurements were made using Leuning passive shuttles (Leuning et al., 1985). A schematic diagram of the shuttle from Leuning et al. (1985) can be seen in Figure 6.1 and the shuttle used in the current experiment can be seen in Plate 1. The shuttle consists of an inverted funnel as an entrance nozzle, a cylindrical body, and a base containing a stainless steel disc with a hole punched out (to control the air flow through the shuttle), a pair of fins (to ensure the shuttle always points into the wind) and mounting pivots for mounting the shuttle onto the mast in the field (Plate 6.1). The cylindrical body consists of a stainless steel sheet coiled and attached to a sealed central tube (Plate 6.2).

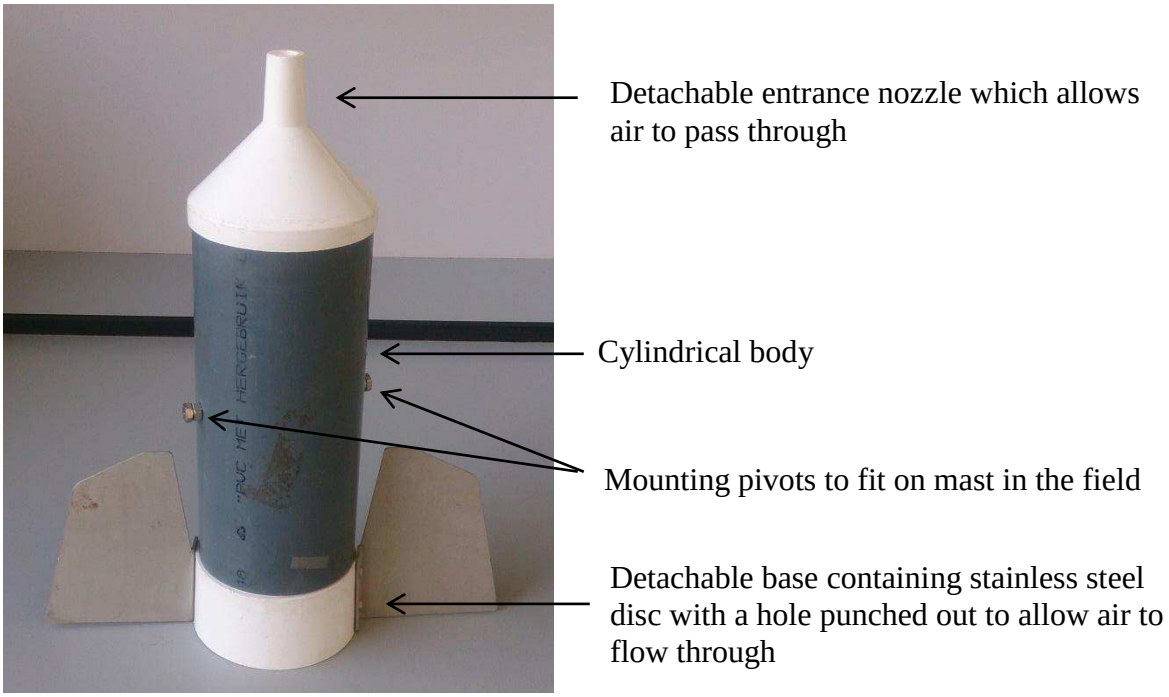


Plate 6.1 Passive sampler for measuring NH_3 emissions consisting of a detachable entrance nozzle, cylindrical body, mounting pivots to attach onto mast in the field and a base containing a stainless steel disc with a hole punched out

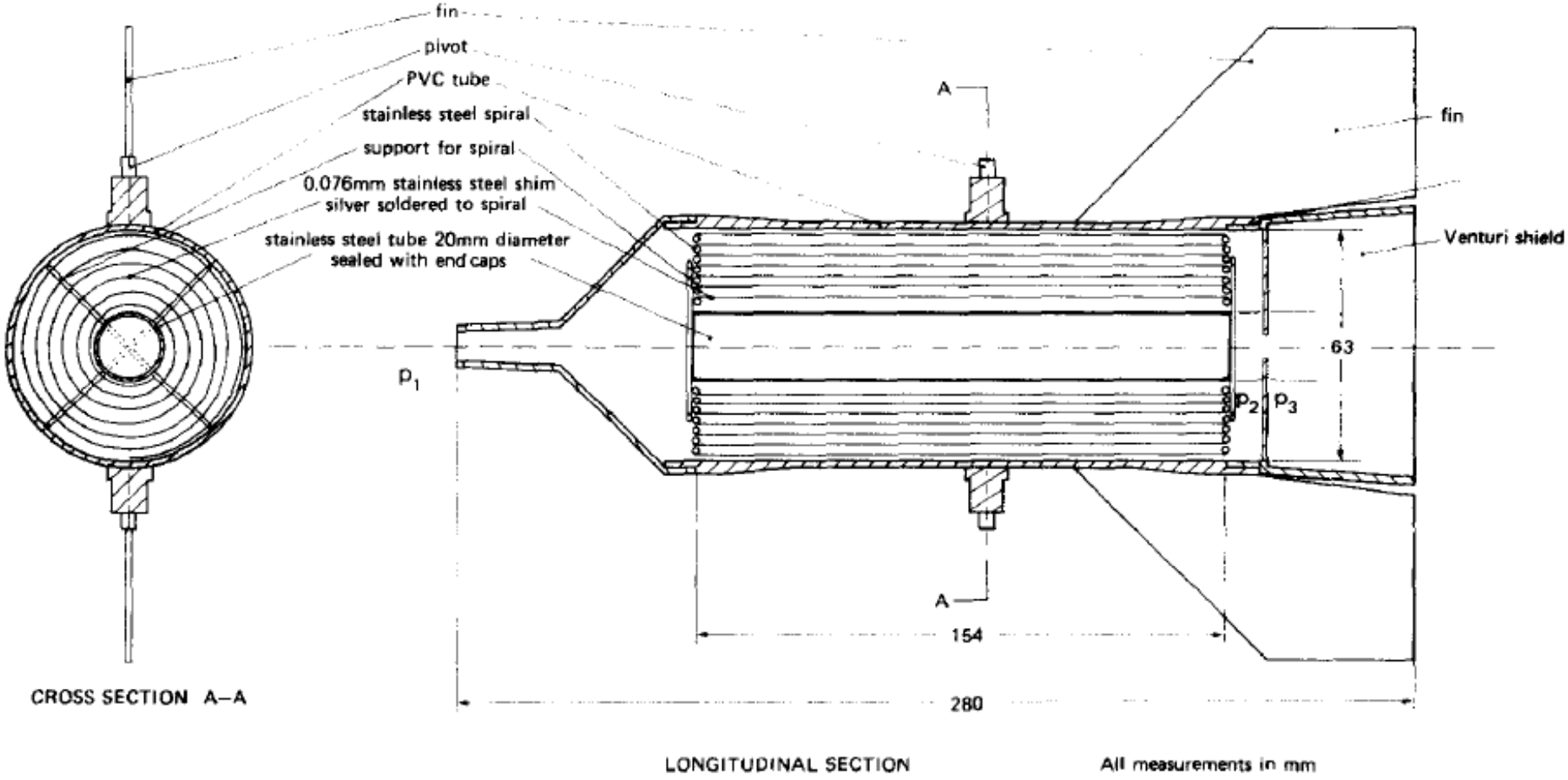


Figure 6.1 Schematic diagram of passive ammonia sampler (Leuning et al., 1985)

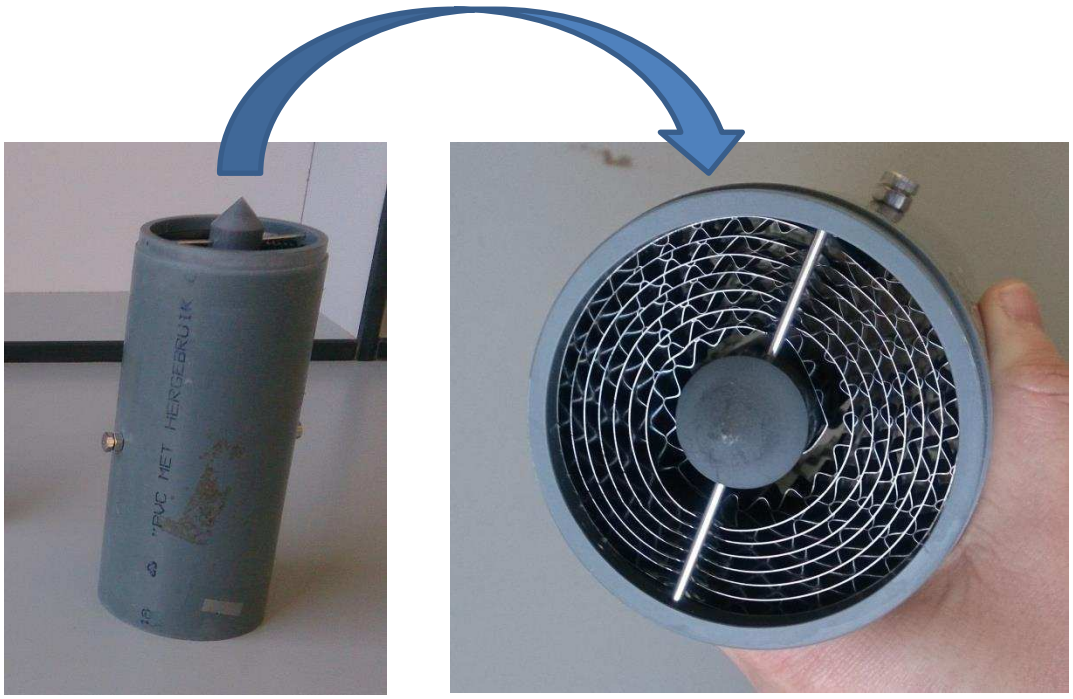


Plate 6.2 Cylindrical body of passive shuttle for measuring NH_3 emissions, consisting of a stainless steel sheet coiled and attached to a sealed, central tube

6.3.4.1 Ammonia shuttle charging

All shuttle pieces were washed and dried before use. A sealed base (i.e. no hole in the bottom) was used when charging shuttles with oxalic acid, and was attached to the cylindrical body with a funnel attached on top. Using a graduated cylinder 30ml of acetone was carefully poured into the shuttle and sealed with a rubber bung. The shuttle was then shaken for 30 seconds to ensure that each part of the stainless steel sheet was coated with acetone. The rubber bung was removed and the excess acetone was then poured out into a waste bottle. The second step involved measuring out 30ml of 3% oxalic acid made up in acetone into a graduated cylinder and carefully pouring it into the shuttle. This was then sealed again with the rubber bung and shaken for 1 minute to ensure each part of the stainless steel sheet was coated with acid. The rubber bung was removed and the excess acid was poured into a waste bottle. The base and funnel were then removed and the shuttle was then left to dry in a fume cupboard. Once dry, a base and funnel were attached

to the shuttle. The base was attached to ensure the fins were aligned with the mounting pivots on the side of the shuttle to ensure that the fins would be vertical when the shuttle was mounted onto the mast in the field. The holes in the funnel and the base were covered with insulating tape and each join was sealed with insulating tape to ensure an airtight seal. The shuttles were then stored at 4° until measurements began.

6.3.4.2 Ammonia shuttle installation in the field

In the field, shuttles were installed on a stainless steel mast 0.6m high in the centre of a fertilised circle measuring 10m diameter (Plate 3). The mounting pivots on the shuttle were installed onto jaws on the mast to allow the shuttle to move freely in the wind and the fins allowed the shuttle to always point into the wind. After fertiliser application shuttles were installed immediately (day 0) and for year 1 were changed on day 1, 3, 6, 9 and removed on day 20 and for year 2 were changed on day 1, 2, 4, 7, 9, 12 and removed on day 19. When installed in the field, the tape covering the hole in the funnel and the base was removed to allow air to pass through the 3% oxalic acid coated cylinder (i.e. acid trap) which captured NH_3 from the air as NH_4^+.

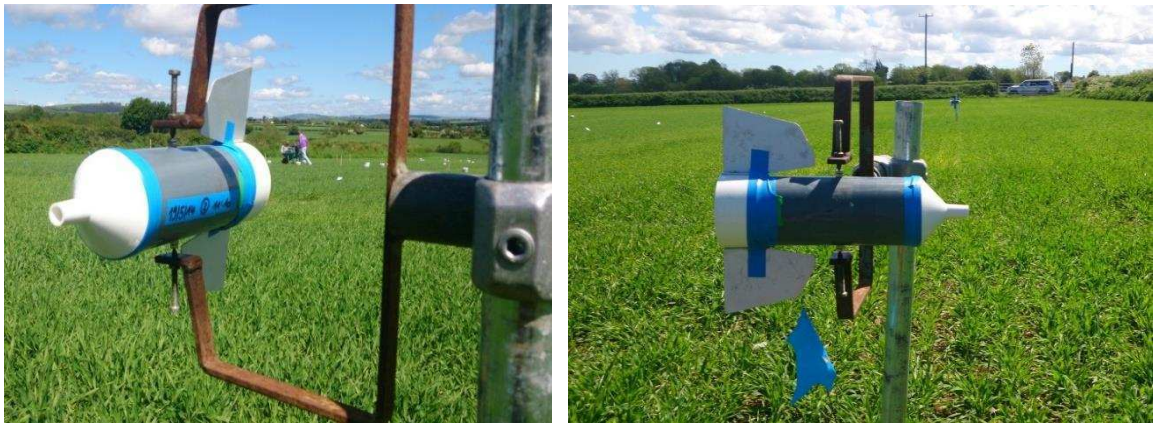


Plate 6.3 Passive shuttles used for NH_3 measurements installed in the field

6.3.4.3 Ammonia shuttle extraction and chemical analysis

When changed in the field, shuttles were sealed with plastic tape and returned to the lab for extraction. The base was removed and replaced with a sealed base (i.e. no hole in the bottom). Using a graduated cylinder 30ml of deionised water was carefully poured into the shuttle and a rubber bung was placed in the funnel to seal. The shuttle was then shaken for one minute to ensure all parts of the stainless steel sheet were washed with deionised water. The sample was then poured into a sample vial and the shuttle was shaken downwards to remove as much solution as possible. Chemical analysis of NH_4^+ was determined colorimetrically using an Aquakem 600A (Aquakem 600A, 01621, Vantaa, Finland). Results shown are expressed as NH_3 concentrations.

6.3.4.4 Climatic analysis

A weather station was located close to both field sites where average daily temperatures (°C) and total daily rainfall (mm) were recorded. Wind speed anemometers were installed in 2014 for measuring wind speed and wind direction. However, the wind data collected was not sufficient to incorporate the NH_3 concentrations into modelling approaches such as the backward lagrangian stochastic modelling. Therefore, the NH_3 concentrations were used as a relative comparison of the N fertiliser formulations, as an indicator of potential NH_3 emissions.

6.3.5 Statistical analysis

Statistical analysis was conducted using the PROC MIXED procedure in SAS 9.3 (2002-2010, SAS Institute Inc., Cary, NC, U.S.A.) for testing cumulative NH_3 concentration

differences between N fertiliser formulations. Significant differences between N fertiliser formulations were determined according to the F-protected least significant difference test ($P < 0.05$). The analysis used separate variances for each site year and treated site year as a block with replications nested within site year to give a total of 6 replicates.

6.4 Results

6.4.1 Weather Conditions

There was no rainfall for five days after fertiliser application in any site year. After five days there was 9.1mm rainfall at JC 2014 (Figure 6.2a), 10.8mm rainfall at MT 2014 (Figure 6.3a) and 1mm rainfall at MT 2015 (Figure 6.4a) followed by a further 6.4mm the day after. MT 2015 had the highest rainfall over the measurement period with 95.2mm rainfall compared to 37.9 in JC 2014 and 51.4 in MT 2014. Temperatures at MT 2014 and JC 2014 were above 9.5°C every day after fertiliser application. Temperatures at MT 2015 were lower with 9.4°C at fertiliser application and declining to 4.6°C 7 days later. Temperatures increased after this to 11.1°C 9 days later.

6.4.2 Temporal NH_3 concentrations

Temporal NH_3 concentrations (daily integrated values (mg L^{-1})) showed that urea had a larger peak in NH_3 concentrations than CAN and urea + NBPT. This was most pronounced at JC in 2014 with NH_3 concentrations from urea rep one (Figure 6.2b) being 5.64 mg L^{-1} compared to 0.68 mg L^{-1} from CAN and 0 mg L^{-1} from urea + NBPT, and urea rep two (Figure 6.2c) having 1.86 mg L^{-1} compared to 0.67 mg L^{-1} from CAN and 0 mg L^{-1} from urea + NBPT two days after fertiliser application. Higher NH_3 concentrations from urea were also evident at MT 2014 with 0.73 mg L^{-1} from rep one (Figure 6.3b) compared to

0.07 mg L^{-1} from CAN and 0.10 mg L^{-1} from urea + NBPT and urea rep two (Figure 6.3c) with 2.86 mg L^{-1} compared to 2.49 mg L^{-1} from CAN and 2.79 mg L^{-1} from urea + NBPT five days after fertiliser application. Higher concentrations from urea were also observed at MT 2015 with 0.49 mg L^{-1} from rep one (Figure 6.4b) compared to 0.18 mg L^{-1} from CAN and 0.29 mg L^{-1} from urea + NBPT and 1.48 mg L^{-1} from rep two (Figure 6.4c) compared to 0.11 mg L^{-1} from CAN and 0.37 mg L^{-1} from urea + NBPT 11 days after fertiliser application.

6.4.3 Cumulative NH_3 concentrations

The main effects of site year, rep (site year) and treatment on NH_3 concentrations were all significant ($P<0.05$) (Table 6.2). Cumulative NH_3 concentrations were calculated by subtracting the unfertilised control NH_3 concentrations from each fertiliser formulation and are expressed in mg L^{-1} and are shown in Figure 6.5. The highest NH_3 concentrations were from the urea treatment with 14.43 mg L^{-1} and was significantly higher than CAN with 11.62 mg L^{-1} and urea + NBPT with 11.31 mg L^{-1} (Figure 6.5). There were no differences between CAN and urea + NBPT on NH_3 concentrations (Figure 6.5).

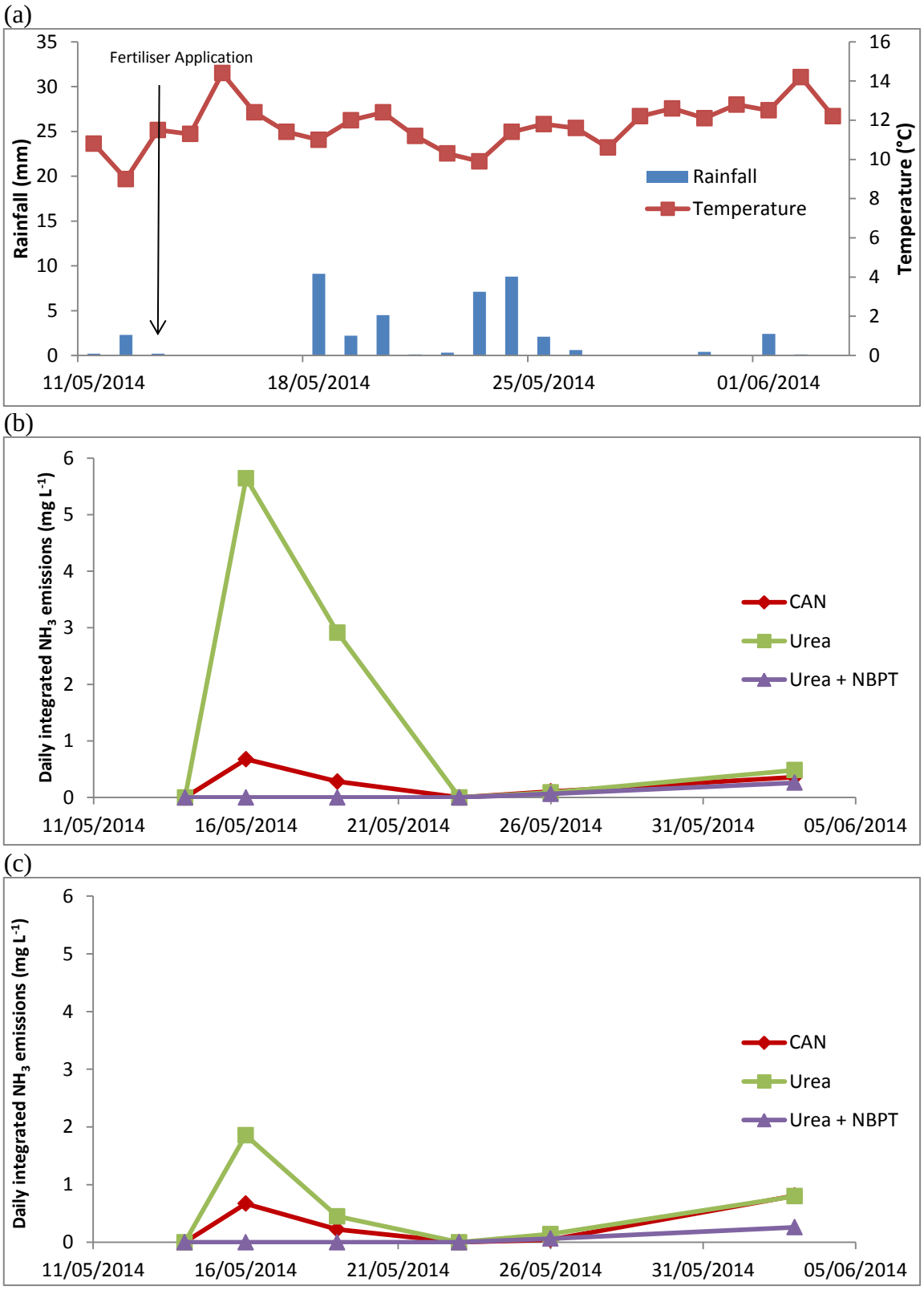
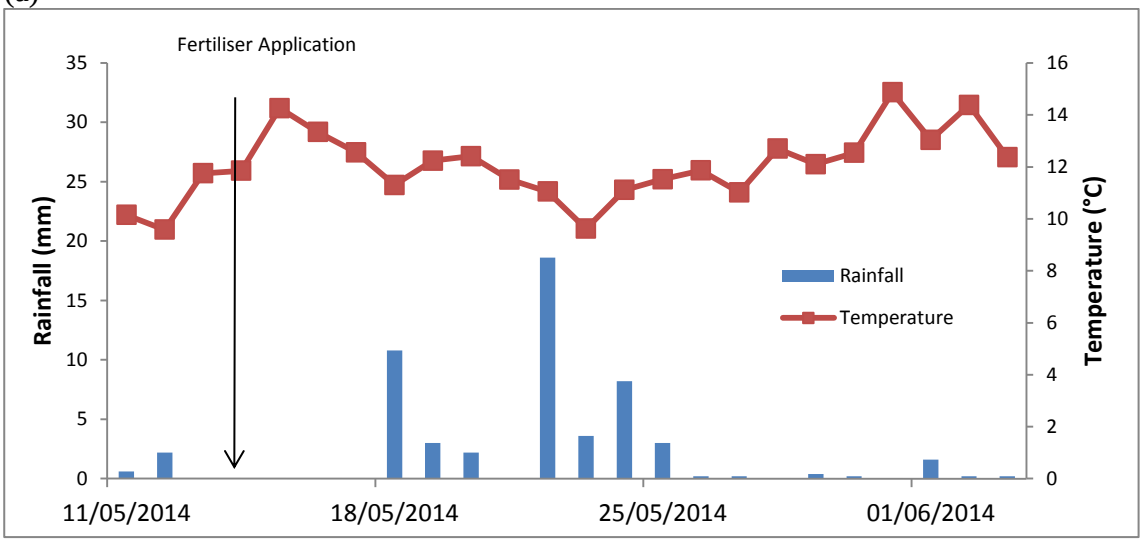
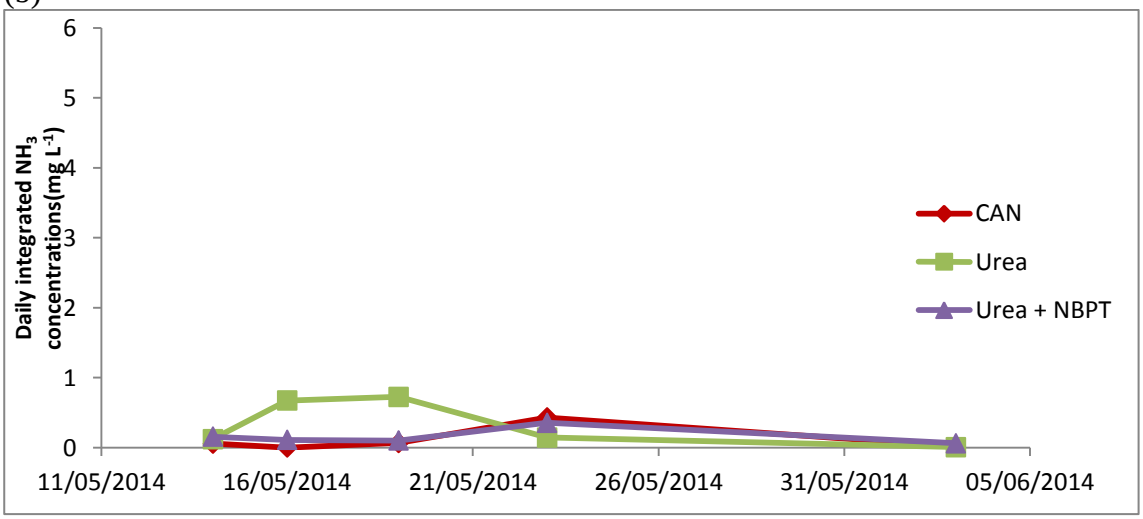


Figure 6.2 JC 2014 NH_3 concentrations. (a) total daily rainfall (mm) and average daily temperature (°C) and (b) daily integrated NH_3 concentrations (mg L^{-1}) for JC 2014 rep 1 and (c) daily integrated NH_3 concentrations (mg L^{-1}) for JC 2014 rep 2

(a)



(b)



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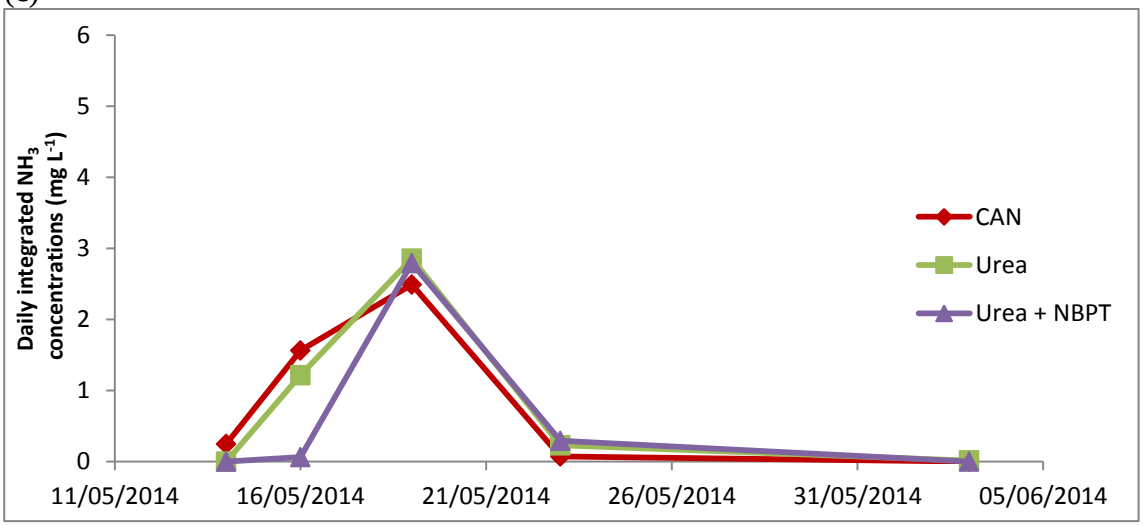
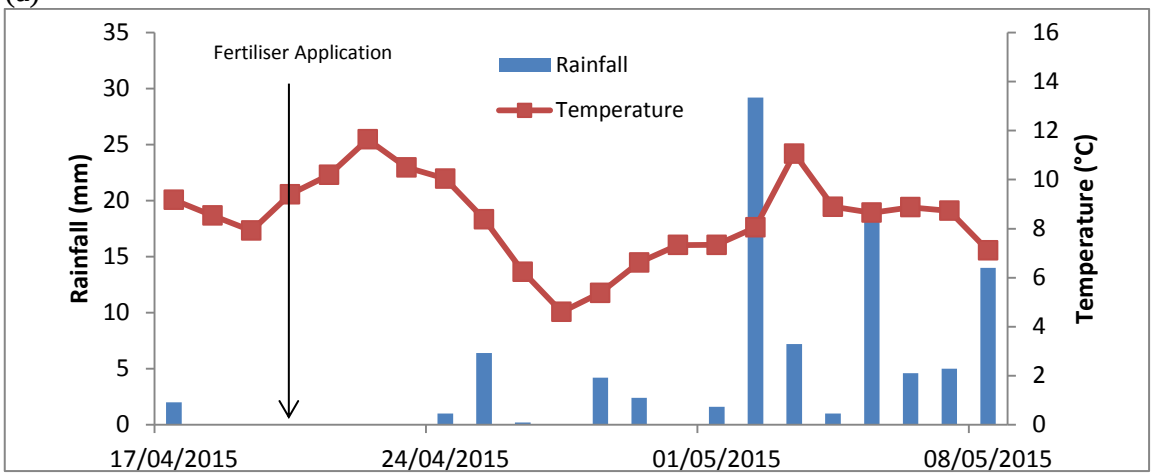
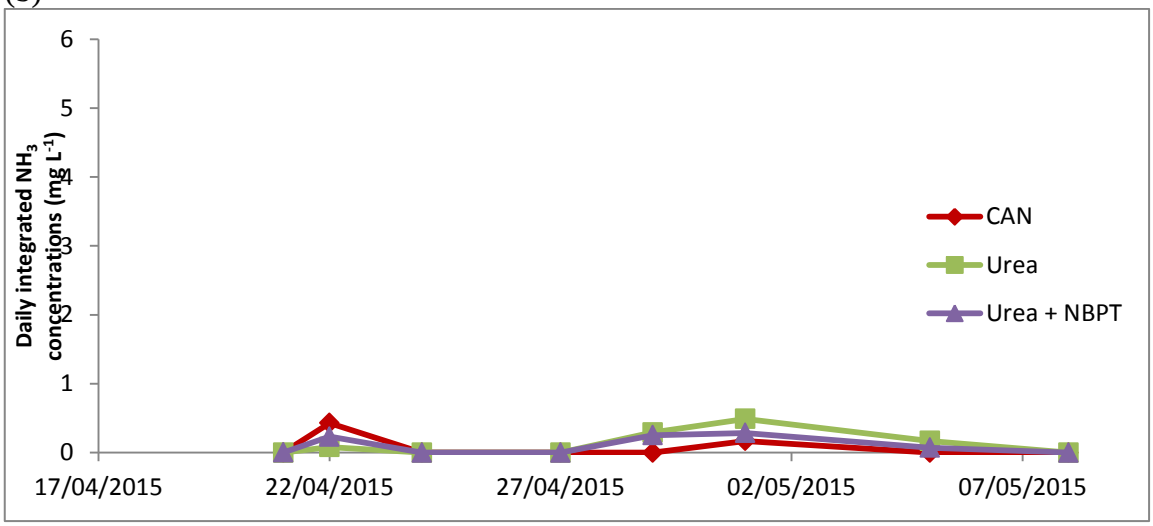


Figure 6.3 MT 2014 NH_3 concentrations. (a) total daily rainfall (mm) and average daily temperature (°C) and (b) daily integrated NH_3 concentrations (mg L^{-1}) for MT 2014 rep 1 and (c) daily integrated NH_3 concentrations (mg L^{-1}) for MT 2014 rep 2

(a)



(b)



(c)

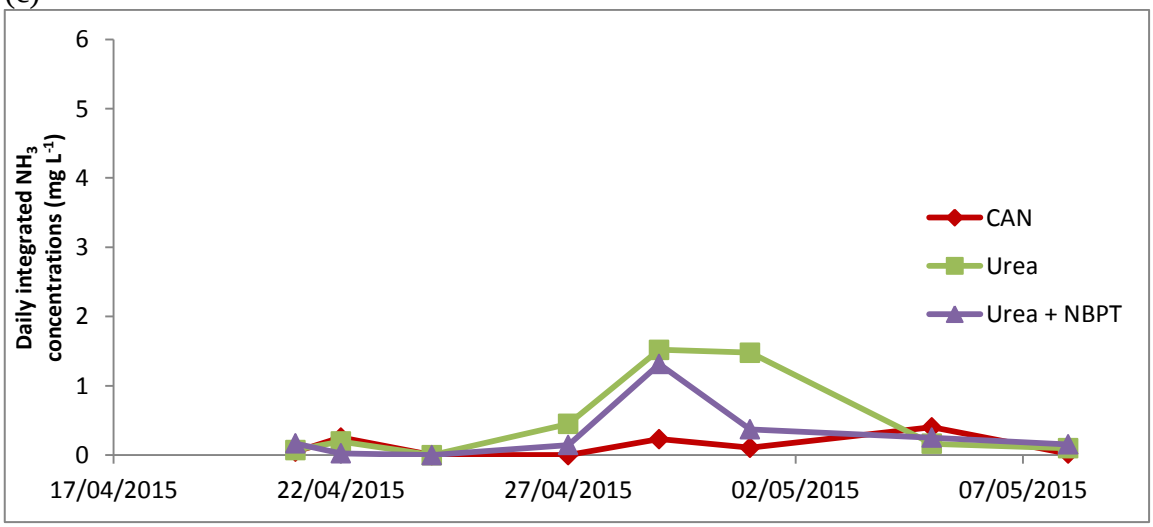


Figure 6.4 MT 2015 NH_3 concentrations. (a) total daily rainfall and average daily temperature (°C) and (b) daily integrated NH_3 concentrations (mg L^{-1}) for MT 2015 rep 1 and (c) daily integrated NH_3 concentrations (mg L^{-1}) for MT 2015 rep 2

Table 6.2 Significant effects and mean cumulative NH_3 concentrations as affected by N fertiliser formulations

Main Effects	**NH_3 emissions**
	P value
Site year	0.0023
Rep (site year)	<0.0001
N fertiliser formulation	0.0290

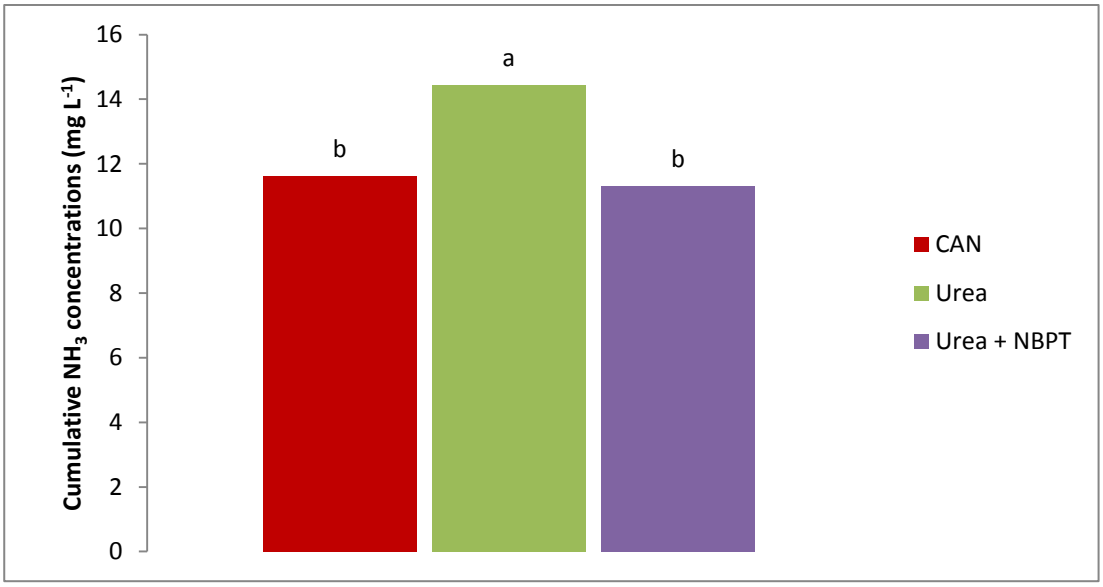


Figure 6.5 Cumulative NH_3 concentrations from different N fertiliser formulations
*different letters represent significant differences between fertiliser formulations using F protected LSD test (P<0.05)

6.5 Discussion

6.5.1 Temporal pattern of NH_3 concentrations

The highest NH_3 concentrations occurred within three days at JC 2014, within five days at MT 2014 and within eight days at MT 2015. The highest losses observed across the three site years were observed at JC 2014. The SMD at JC 2014 was 10.9mm that day of N fertiliser application showing that only 10.9mm rainfall was required to bring the soil to field capacity. Urea hydrolysis occurs in the presence of water (equation 2.6 in section 2.6.4 in chapter 2) and studies have shown that applying urea to wet soil can promote NH_3 losses (Bouwmeester et al., 1985). McInnes et al. (1986) reported that small amounts of rainfall after application can promote loss and Forrestal et al. (2015) showed that rainfall losses of 0.3mm promoted NH_3 losses which could explain the higher losses at JC 2014 with 0.2mm rainfall the day of application. The 0.2mm rainfall coupled with wet soil at the time of application could explain the higher losses at JC 2014 compared to MT 2014 and MT 2015.

At MT 2014 the highest NH_3 concentrations occurred five days after fertiliser application. On the fifth day a rainfall event of 10.8mm occurred and after this NH_3 concentrations were low, with levels close to zero. This indicates that the rainfall washed the urea below the soil surface which resulted in minimal NH_3 concentrations thereafter. This is in agreement with other studies which have shown that rainfall after application can wash urea below the soil surface and reduce NH_3 losses (Sommer et al., 2004; Holocomb et al., 2011; Forrestal et al., 2015).

At MT 2015 the highest NH_3 concentrations were observed eight days after fertiliser application. There was no rainfall for the four days before application and Terman (1979) in Bhogul et al. (2003) showed that urea applied to air-dry soil does not hydrolyse and

therefore NH_3 emissions aren't produced. This could explain why concentrations did not peak until eight days after application. In addition temperatures decreased to 4.6°C after N fertiliser application and urea hydrolysis rates are lower at lower temperatures (Jones et al., 2007). Once temperatures began to increase, so too did NH_3 concentrations and after rainfall events NH_3 concentrations decreased to levels close to zero.

6.5.2 Effect of rainfall on NH_3 concentrations

Rainfall or irrigation after fertiliser application can reduce NH_3 emissions and is considered a mitigation strategy (Sommer et al., 2004). Holcomb et al. (2011) reported that 14.6mm of irrigation immediately after urea fertiliser application reduced urea losses by 90%. Forrestal et al. (2015) reported that 5.8mm rainfall 1 day after application reduced NH_3 emissions to 8% of the N applied compared to losses of 25.1% of the N applied with no rainfall. In the current study rainfall occurred 5 days after fertiliser application at MT 2014 and 4 days after application at MT 2015. AT JC 2014 there was 0.2mm rainfall the day of application and then 5 days later 9.1mm rainfall occurred. McInnes et al. (1986) reported that small amounts of rainfall, such as the 0.2mm in JC 2014 enhances NH_3 emissions rather than reduces it. This may explain the higher NH_3 concentration peaks that occurred immediately at JC 2014 compared to MT 2014 and MT 2015. The peaks at MT 2014 and 2015 corresponded with rainfall events and NH_3 concentrations were low compared to JC 2014. Rainfall amounts were above 6.4mm indicating that this was sufficient to wash NH_4^+ from solution into the soil and minimise losses.

6.5.3 Effect of fertiliser formulation on NH_3 emissions

This study showed that urea produces significantly higher NH_3 concentrations compared to CAN. Using urea + NBPT significantly reduced NH_3 concentrations compared to urea and had similar levels to CAN. This is in agreement with other studies that have found urea + NBPT to reduce NH_3 emissions compared to urea (Sanz-Cobena et al., 2008; Forrestal et al., 2015). The results from this study were a relative comparison and were not quantified but other studies have shown urea + NBPT to reduce emissions using urea + NBPT from 28% up to 87% (Rawluk et al., 2001; Watson et al., 2008; Sanz-Cobena et al., 2008, 2011; Forrestal et al., 2015). Forrestal et al. (2015) demonstrated that urea + NBPT reduced NH_3 emissions to 8% of the N applied compared to 25% of the N applied with urea in Irish grassland systems. Sanz-Cobena et al. (2008, 2011) showed a 57% reduction in NH_3 emissions using urea + NBPT compared to urea in a Mediterranean sunflower crop. In addition a meta-analysis by Pan et al. (2016) showed that on average urea + NBPT reduced NH_3 emissions by 54% compared to urea.

Previous studies have also shown that there was little impact on ammonia loss in terms of the amount of NBPT on the granule once application rate was above (250 mg kg^{-1} NBPT concentration (Rawluk et al. 2001; Watson et al. 2008). However, a significant drop in efficacy was observed at 25^{o}C compared to 15^{o}C. In general, ammonia emissions may be considered to be higher on arable soils compared to grassland in Ireland as the majority of tillage is on free-draining sandy brown earth soils. Higher emissions (and reduced NBPT efficacy) have generally been observed on sandy soils compared to heavier soils, which may be due to a lower capacity for retention of NH_4^+ and larger particle size (Rawluk et al., 2001; San Francisco et al. 2011). Also the impact of growth stage at which application takes place cold be important, as emissions under higher more developed canopies tend to be reduced due to alterations in microclimate at the soil surface (Meade et al., 2011).

6.6 Conclusions

Overall, this study shows that using urea + NBPT can reduce NH_3 emissions compared to urea on spring barley in Ireland. The results from this study are in agreement with other national and international studies showing that urea stabilised with the urease inhibitor NBPT reduces NH_3 emissions. The results in this study were a relative comparison and further research using micrometeorological techniques for quantitative analysis on NH_3 emissions are needed in the context of national commitments for reducing NH_3 emissions.

Chapter 7 - Effect of N fertiliser formulation on spring barley grain yield and crop N uptake: CAN versus urea with and without N stabilisers

7.1 Summary

The alteration of N fertiliser formulation is a potentially highly effective mitigation strategy for reducing environmental losses of N (including N_2O and NH_3 emissions and NO_3^- leaching to ground and surface waters) without impacting on productivity. As such, it is important to assess the potential effects that new N fertiliser sources will have on grain yield and quality which directly effects the profitability and economic sustainability of the cropping system as well as the marketability of the grain. Overall, improving fertiliser NUE is important agronomically, environmentally and economically. In this study, the effect of six fertiliser formulations on grain yield and N uptake of spring barley were studied on two contrasting sites over three years. The six fertiliser formulations were assessed at a rate of 100 kg N ha^{-1} which was less than the typical optimum rate in all site years. Results showed that grain yield was not affected by changing N fertiliser source and was similar regardless of the N source used. There were differences in the N uptake between fertiliser formulations with urea + NBPT having the highest N uptake. This was significantly higher than urea but not significantly different than CAN. This shows that there is scope for switching N fertiliser source for spring barley from traditionally used CAN to urea + NBPT while maintaining yield and potentially increasing crop N uptake. The impact of these N fertiliser formulations on other crop yields (i.e. wheat, oats) under varying soil types and conditions is warranted by future research.

7.2 Introduction

Nitrogen fertiliser is one of the largest input costs for arable farmers in Ireland and is essential for achieving high crop yields. Globally, urea is the most used N fertiliser source accounting for approximately 56% of the world market (IFA, 2013). However, in Ireland and Europe, calcium ammonium nitrate (CAN) or ammonium nitrate (AN) is the N fertiliser source of choice. In 2008, CAN comprised 61% of all N fertiliser used on cereal crops with urea accounting for only 3% and the remainder compounds (Lalor et al., 2010). For spring barley 55% of the N fertilisers were CAN and the remainder consisted of compound N fertilisers with 0% urea used (Lalor et al., 2010). Although urea (46% N) is cheaper per unit of N than CAN (27% N), studies have shown reduced cereal grain yields with urea compared to CAN (Devine and Holmes, 1963; Gately, 1994; Conry, 1997) due to both volatilisation and poor ballistics and consequently farmers use CAN for achieving consistent grain yields year on year. The application of N fertilisers to soils contributes to N losses to the environment including nitrous oxide (N_2O) emissions, ammonia (NH_3) emissions and nitrate (NO_3^-) leaching (Cameron et al., 2013). These losses represent an economic loss to farmers and have implications for water quality (via NO_3^- leaching), GHG emissions and air quality (due to ammonia volatilisation). Nitrogen stabilisers, including urease and nitrification inhibitors, have received attention recently (Forrestal et al., 2015; Roche et al., 2016; Harty et al., 2016) in terms of mitigating environmental losses of N but it is necessary to assess the potential effects these products have on crop yields and nitrogen use efficiency (NUE). The effect of N fertiliser on grain yield and quality is of particular importance to barley (*Hordeum vulgare* L) as it is one of the most important cereal crops in the world. Approximately 55 million hectares of barley is produced worldwide with a global production of approximately 132 million tons (Akar et al., 2004). Approximately 70% of global barley production is used for animal feed with the

remaining 30% used for malting purposes (Akar et al., 2004). Approximately 62% of global barley production is in Europe and Ireland is the third highest yielding country on a per hectare basis (FAO, 2016b) within the EU.

Urea based N stabilisers are formulated to reduce environmental N losses including N_2O emissions, NH_3 emissions and NO_3^- leaching. When urea is applied to soil it is initially hydrolysed converting urea to ammonium and variable levels of NH_3 may be lost to the atmosphere. Between 10 and 20% of urea fertiliser applied can be lost as NH_3 (Harrison and Webb, 2001) which could result in reduced yields compared to CAN. The addition of a urease inhibitor to urea slows down the rate of urea hydrolysis, thereby delaying the transformation of urea to NH_4^+ in the soil and reducing NH_3 losses. The most popular urease inhibitor is N-(n-butyl) thiophosphoric triamide (NBPT (referred to as n-BTPT in some studies)). Several studies have shown a reduction in NH_3 loss with the addition of NBPT compared to using urea alone (Watson et al., 2009; Forrestal et al., 2015). The addition of a nitrification inhibitor to urea slows down conversion of ammonium (produced as a result of urea hydrolysis) to nitrate via nitrification. Nitrate is an anion and is very mobile in soil and, if not taken up by the plant, can be easily lost through NO_3^- leaching or through denitrification producing gaseous N forms. The most popular nitrification inhibitor is dicyandiamide (DCD) and has been shown to reduce N_2O emissions compared to CAN in grassland and cereal systems (McTaggart et al 1997; Misselbrook et al 2014; Roche et al 2016; Harty et al 2016a).

The combination of a urease and nitrification inhibitor to urea can have the added benefit of slowing down both urea hydrolysis and nitrification and reducing losses even further than when using either inhibitor individually (Harty et al., 2016a). Altering fertiliser form and/or rate may be a key abatement strategy for reducing N_2O emissions from agriculture

but it must not negatively impact yields. In this study, grain yield, N uptake and protein content were measured from spring malting barley. In order for barley to be accepted for malting purposes it needs to have a protein content of between 9.5 and 11.5% (at harvest – usually at 15% moisture content). An adequate N supply is important for grain protein content but grain protein content is variable between sites and years (Hackett, 2014). In order to assess changing N fertiliser source for malting barley, grain protein content must be evaluated. The aims of this study were to quantify the effect of different N fertiliser forms on spring barley grain yield, protein content and N uptake. The hypothesis tested was: switching N fertiliser formulation from CAN to urea with N stabilisers will not negatively impact yield, N uptake or protein content.

7.3 Materials and Methods

7.3.1 Site description

Field experiments were conducted on a free-draining loam soil located in Marshalstown (MT), Co. Wexford and a moderately draining sandy loam soil located in Johnstown Castle (JC), Co Wexford. Site locations and soil characteristics for both experimental field sites can be seen in Table 3.1 in chapter 3. The MT site had been in long term arable production for approximately 20 years with continuous spring barley production since 2007. The JC site had been in arable production for maize silage (Zea mays) in the three years prior to commencing this experiment. Prior to this it was in permanent grassland. The JC site received organic manure annually while it was in grassland and also when cropped with maize (Zea mays).

7.3.2 Crop husbandry

The spring barley (*Hordeum vulgare L*) was *CV*. 'Sebastian' which is a Danish malting variety with short straw length and a good disease resistance. The site was ploughed (20 - 30cm depth) in February in 2013 and March in 2014 and 2015. The spring barley was planted at a seeding rate of 169 kg ha^{-1} in April in all three years and was harvested at maturity. The study ran from April 2013 to September 2015 generating three years of data. Each year basal P, K and S were applied to the soil, according to the Teagasc Green Book of nutrient advice (Coulter and Lalor, 2008) to prevent nutrient deficiencies from occurring. A robust pesticide programme was applied to the crop to control weeds, pests and diseases as per standard agronomic practice for spring barley crops (Teagasc, 2016b).

7.3.3 Experimental Design

The overall study is split into two experiments, called experiment 1 and experiment 2 from here on in. A randomised block design was used with five replicates of each treatment. In experiment 1 four N fertiliser formulations which included N stabilisers were used, as well as an unfertilised control. The N stabilisers evaluated were the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT (also called n-BTPT in some studies)) and the nitrification inhibitor dicyandiamide (DCD). The four N fertiliser formulations were (i) CAN, (ii) Urea (iii) Urea + the urease inhibitor NBPT (source Agrotain™ 660 ppm) (iv) Urea + the nitrification inhibitor DCD and an unfertilised control. Experiment 2 included the same four N fertiliser formulations as experiment 1 and an unfertilised control but also included two extra N stabilisers which were urea + NBPT + DCD and urea + the urea stabiliser Maleic-Itaconic Co-polymer (MICO (trade name Nutrisphere®). Each plot measured 12 x 2.5m. Fertiliser was applied at a rate of 100 kg N ha^{-1} which was an N responsive rate where differences between treatments due to N losses would be expected to be identifiable.

Fertiliser N was applied in two split applications. The first split comprised 30 kg N ha^{-1} and was surface applied within seven days of planting the barley. The second split comprised the remainder fertiliser (70 kg N ha^{-1}) and was applied during early to mid-tillering (GS 22-25 (Zadocks.198x). Dates of fertiliser application can be seen in Table 3.3 of chapter 3.

7.3.4 Crop Sampling

Crop N uptake sampling was conducted in 2014 and 2015 and commenced each year at GS 30 - 37 (stem-extension) and was conducted again at GS45 - 50 (booting/awning) and GS 58 (flowering) for all treatments. Plants from four randomly selected 0.5m row lengths within each plot were cut off at ground level and bundled together to form one composite sample for analysis. The samples were then oven dried at 70°C for 76 hours to a constant mass and weighed to determine biomass dry matter (DM) from which DM yield (kg ha^{-1}) was determined. Crop samples were then finely ground through a 1mm metal sieve (C and M Junior Laboratory Mill) and N concentration was determined using the Dumas method on a CN Leco FP 2000 analyser (LECO Corporation, St. Joseph, MI, USA). Immediately prior to harvest, plots were sampled to determine harvest index and plant N concentration. One hundred shoots were taken at random from the plot. The shoots were carefully removed to ensure all senescent plant tissue was retained. Samples from each plot were bulked together to give one composite sample. The samples were oven-dried at 70°C for 76 hours to a constant mass. To capture the grains, they were then threshed from the straw using a custom built grain thresher and grains and straw were ground and analysed for N as above. At the end of the growing season crops were harvested using a Deutz-Fahr plot-combine (SDF Group Treviglo, Italy). The overall plot yields were recorded, adjusted to

15% moisture content and grain protein content was analysed by near infrared spectroscopy (Infratec 1241, Foss A/S, Hillerød, Denmark).

7.3.5 Statistical Analysis

Statistical analysis was conducted using the PROC GLIMMIX procedure in SAS 9.3. Significant differences between N fertiliser formulations were determined according to the F-protected least significant difference test ($P < 0.05$). The two experiments were statistically analysed separately and the N fertiliser formulations in each experiment are shown in table 7.1. The variables included in the model were site year and treatment and their interaction, and these were tested as fixed effects with replicate as a random effect.

Table 7.1 Description of N fertiliser formulations and years in each experiment for grain yield, total crop N uptake and grain protein concentration

Experiment 1 – 2013, 2014, 2015	**Experiment 2 – 2014, 2015**
CAN	CAN
Urea	Urea
Urea + NBPT	Urea + NBPT
Urea + DCD	Urea + DCD
Unfertilised Control	Urea + NBPT + DCD
	Urea + MICO
	Unfertilised Control

7.4 Results

7.4.1 Experiment 1

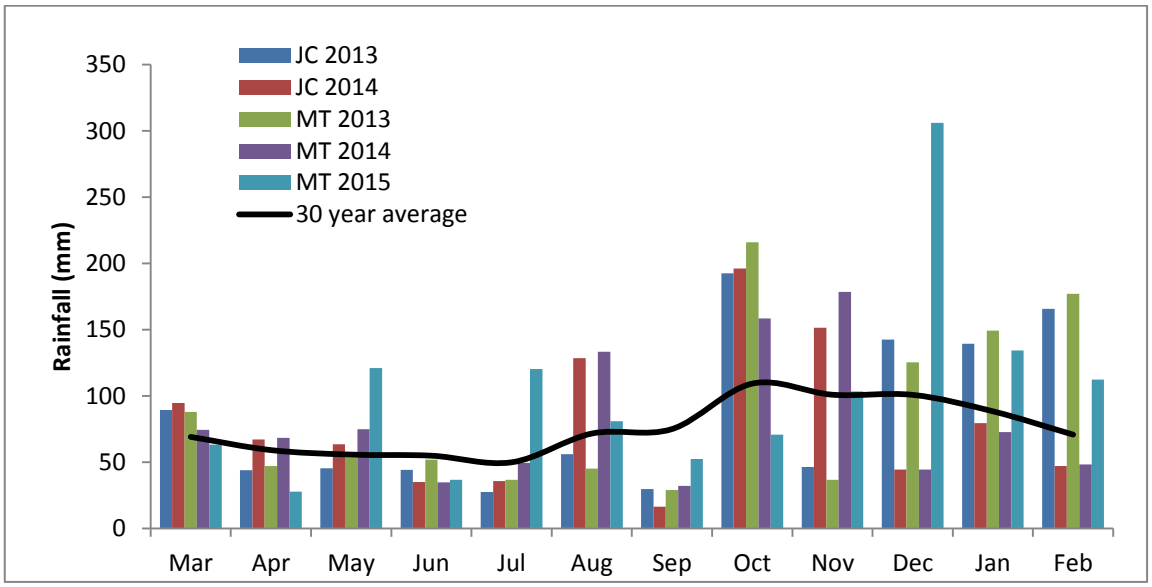
Evaluation of four fertiliser formulations (CAN, Urea, urea + NBPT and urea + DCD) over 5 site years. This experiment includes weather conditions for the growing season, grain yield at harvest, total crop N uptake (N in above ground biomass including grain and straw) and protein percentage.

7.4.1.1 Weather Conditions

Cumulative rainfall amounts for each month and monthly mean temperatures for the five site years in comparison to the 30 year national average are presented in Figure 7.1. There was a large variation in monthly rainfall amounts within and between years, with monthly amounts ranging from 16.3mm (September at JC 2014) to 306.0 mm (December MT 2015). Cumulative rainfall for the growing season (March – August) was below the 30 year average (360.3mm) in JC 2013 with 306.6mm and in MT 2013 with 322.4mm. Cumulative rainfall was above the 30 year average (360.3mm) in JC 2014 with 424.5mm, MT 2014 with 435.2mm and MT 2015 with 449.8mm. The highest rainfall occurred in the winter months (October – February).

Average monthly air temperatures during the growing season (March – August) ranged from 3.8 °C (March at MT 2013) to 17.6 °C (July at MT 2013). Temperatures were close to the 30 year average except for March in JC 2013 and MT 2013 where the 30 year average was 7.5 °C and MT 2013 was 3.8 °C and JC 2013 was 4.2 °C. The highest temperatures occurred in the summer months (June – September) and the lowest temperatures occurred in the winter months (December – March).

(a)



(b)

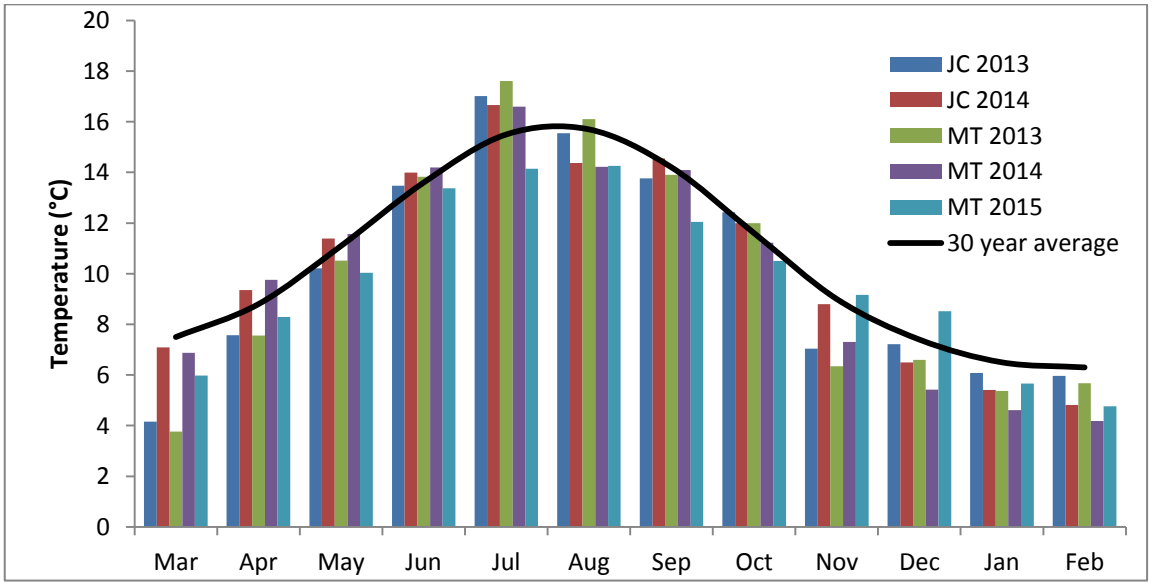


Figure 7.1 Experiment 1. (a) Monthly cumulative rainfall amounts (mm) and (b) monthly mean air temperatures (°C) for the five experimental site years compared to the national 30 year average

7.4.1.2 Grain yield

There was a significant site year by N fertiliser formulation interaction for grain yield (P<0.001) (Table 7.2). All fertiliser formulations produced higher grain yield than the unfertilised control (Table 7.3) and fertiliser formulations were not significantly different to each other. JC produced higher grain yield than MT by approximately 1.5 – 2 t ha^{-1}. On average CAN produced the highest grain yield numerically with 8.61 t ha^{-1} (Table 7.3). CAN relative yield (CRY) was 98% for urea and urea + NBPT and 97% for urea + DCD (Table 7.3).

Table 7.2 Significant effects of N fertiliser formulation and site year and their interaction on grain yield, total crop N uptake and grain protein percentage across five site years (MT 2013, 2014,2015 and JC 2013, 2104).

Effect	**Grain Yield**	**Total crop N Uptake**	**Grain protein percentage**
		P Value	
N fertiliser formulation	<0.0001	<0.0001	0.0467
Site year	<0.0001	<0.0001	<0.0001
N fertiliser formulation * site year	<0.0001	0.2619	0.834

Table 7.3 Grain Yield as affected by N fertiliser formulation in experiment 1

	JC 2013	JC 2014	MT 2013	MT 2014	MT 2015	Average	CRY
	Grain Yield (t ha^{-1})						
CAN	10.12 a	9.77 a	7.29 a	7.72 a	8.14 a	8.61	100%
Urea	9.90 a	9.44 a	7.29 a	7.70 a	8.07 a	8.48	98%
Urea + NBPT	10.16 a	10.15 a	7.69 a	7.66 a	7.79 a	8.48	98%
Urea + DCD	10.23 a	9.56 a	6.96 a	7.05 a	7.77 a	8.31	97%
Control	6.66 b	8.19 b	2.37 b	2.68 b	3.12 b	4.60	

*pooled standard ranged from 0.32 – 0.36

*Different letters represent significant differences between N fertiliser formulations within site years using F protected LSD test (P<0.05)

*URY = urea relative yield

7.4.1.3 Total crop N Uptake

There was no significant two way interaction for total crop N uptake between N fertiliser formulation and site year (P>0.05) but there was a significant N fertiliser formulation effect and a site year effect (P<0.05) (Table 7.2) All fertiliser formulations were significantly higher than the unfertilised control (Figure 7.2). CAN was significantly higher than urea with 149.41 kg N ha^{-1} compared to 135.55 kg N ha^{-1} from urea . Urea + NBPT was not different to CAN and CAN was significantly higher than urea + DCD.

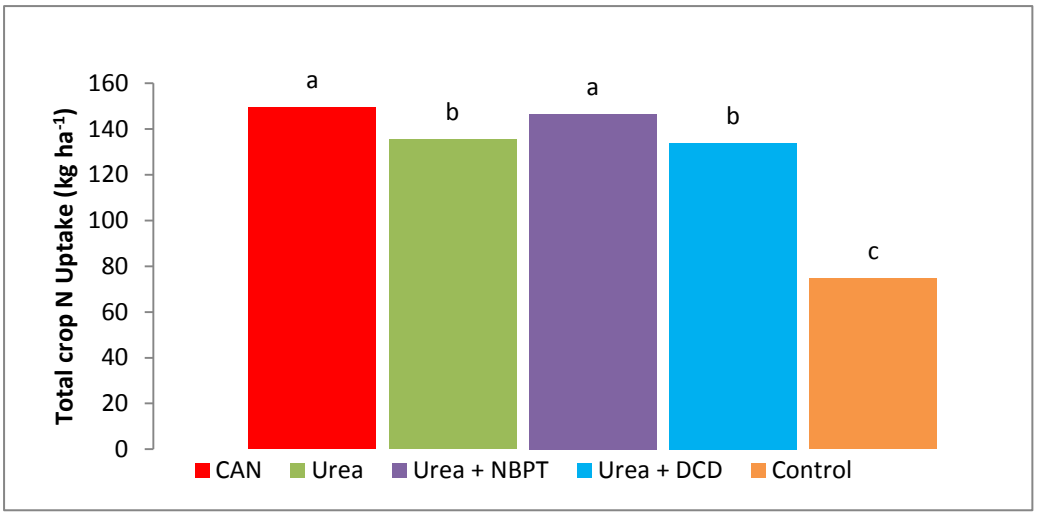


Figure 7.2 Total crop N uptake for different N fertiliser formulations in experiment 1
*Different letters represent significant differences between N fertiliser formulations using F protected LSD test (P<0.05)

7.4.1.4 Grain protein percentage

There was no site year by N fertiliser formulation interaction (P>0.05) for protein percentage but there was a significant N fertiliser formulation effect (P<0.0001) and a site effect (Table 7.2). CAN had the highest protein percentage with 10.16% and this was significantly higher than urea + NBPT with 9.39% and urea + DCD with 9.64% (Figure 7.3). There was no difference between CAN and urea or the unfertilised control.

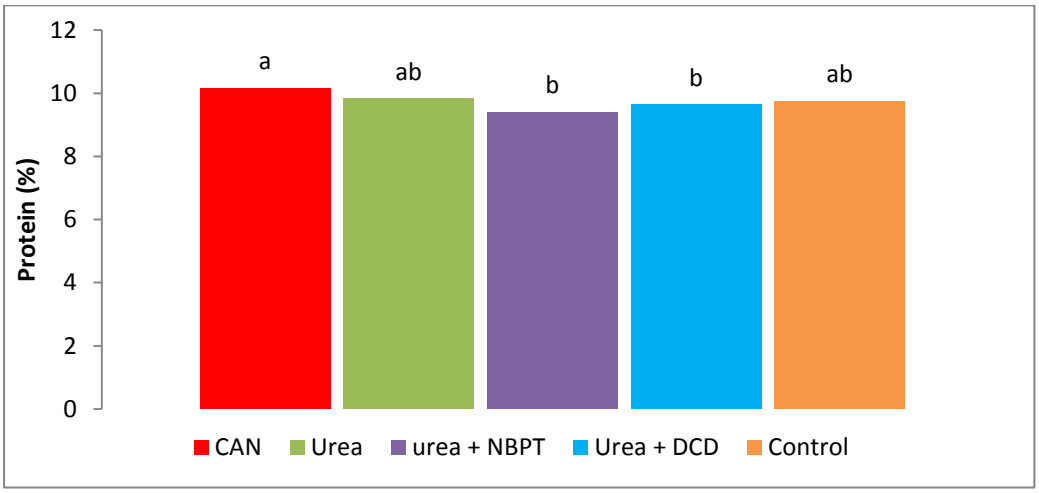


Figure 7.3 Grain protein percentage for different N fertiliser formulations in experiment 1

*Different letters represent significant differences between N fertiliser formulations using F protected LSD test (P<0.05)

7.4.2 Experiment 2

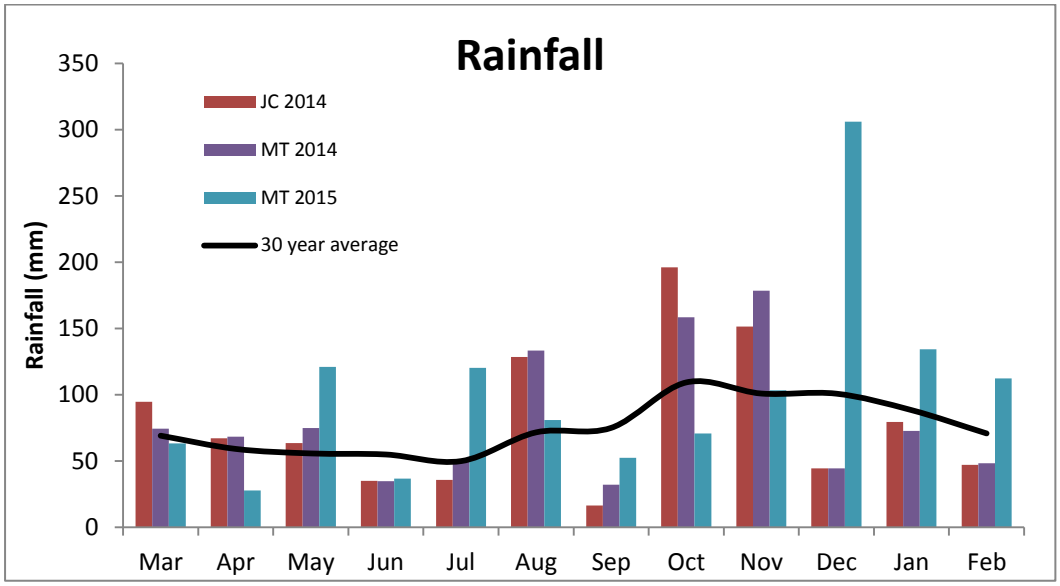
Evaluation of a larger group of N fertiliser formulations (CAN, urea, urea + NBPT and urea + DCD, urea + NBPT + DCD, and urea + MICO) over three site years. This experiment includes weather conditions for the growing season, in season N uptake across three growth stages, grain yield at harvest, total crop N uptake (N in above ground biomass including grain and straw) and protein percentage.

7.4.2.1 Weather Conditions

Cumulative rainfall amounts for each month and monthly mean temperatures for the three site years in comparison to the 30 year national average are presented in Figure 7.4. There was a large variation in monthly rainfall amounts within and between years, with monthly amounts ranging from 16.3 mm (September at JC 2014) to 306 mm (December MT 2015). Cumulative rainfall for the growing season (March – August) was above the 30 year average (360.3mm) in JC 2104 with 424.5mm, MT 2014 with 435.2mm and MT 2015 with 449.8mm. The highest rainfall occurred in the winter months (October – February)

Average monthly air temperatures during the growing season (March – August) ranged from 4.18°C (February MT 2014) to 16.66°C (July JC 2014). Overall, temperatures for all years were very similar to the 30 year average values. The highest temperatures occurred in the summer months (June – September) and the lowest temperatures occurred in the winter months (December – March).

(a)



(b)

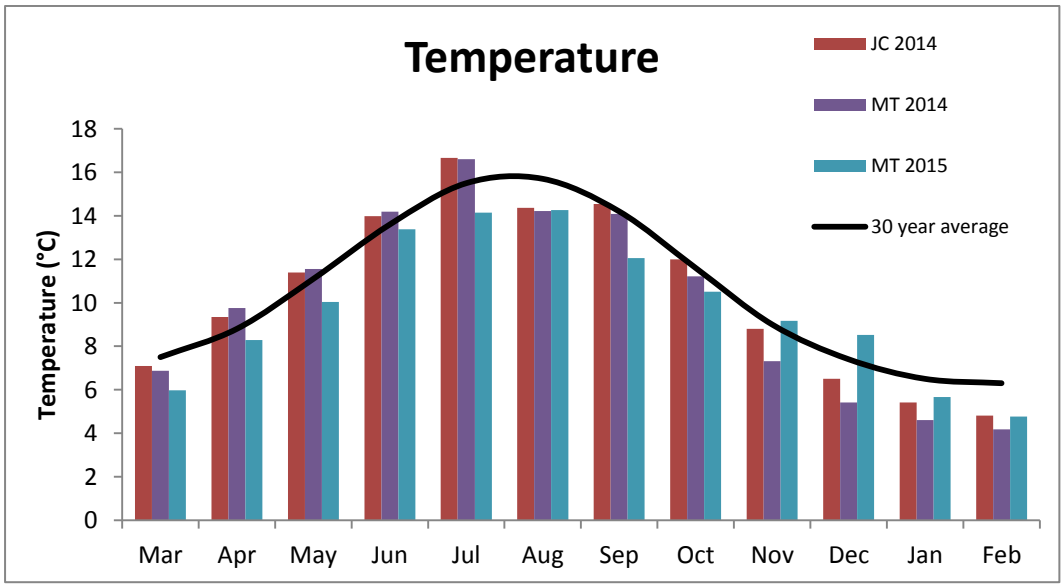


Figure 7.4 Experiment 2. (a) Monthly cumulative rainfall amounts (mm) and (b) monthly mean air temperatures (°C) for the three experimental site years compared to the national 30 year average

7.4.2.2 In Season N Uptake

There was a significant three-way interaction ($P<0.05$) of site year x N fertiliser formulation x crop growth stage (Table 7.4) i.e. different N fertiliser formulations behaved differently at different sites and growth stages.

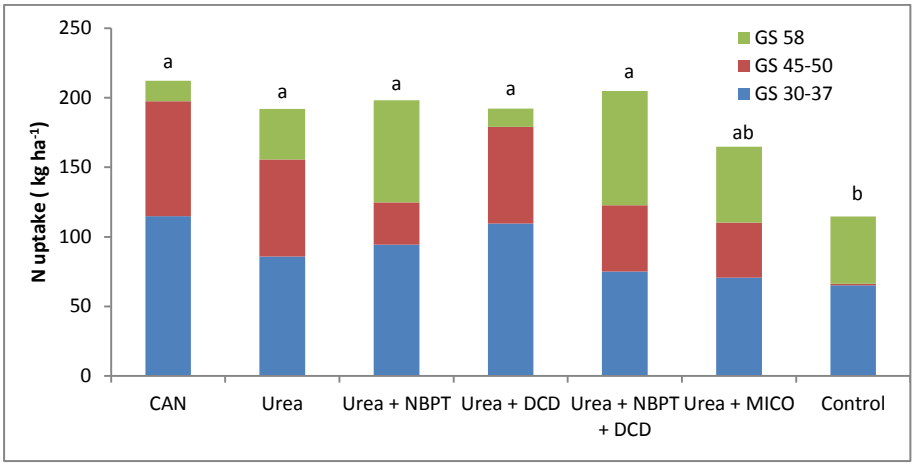
Significant differences in N uptake between N fertiliser formulations within each site year are shown in figure 7.5 at GS 58. In 2014, JC had the highest N uptake across all formulations compared to the other site years (Figure 7.5) with N uptake from CAN of 197.60 kg N ha^{-1} compared to 113.84 kg N ha^{-1} in MT 2014 and 91.97 kg N ha^{-1} in MT 2015. The growth stage with the largest proportion of total N uptake was GS 30 – 37 for all site years and with the exception of JC 2014 the overall formulation differences became apparent at GS 58. The control had the lowest N uptake in all site years which was significantly lower than all N fertiliser formulations except for urea + MICO in JC 2014 and 2015.

CAN had significantly higher N uptake compared to urea in MT 2014 but there were no significant differences between CAN and urea in the other site years. There was no difference between CAN and urea + NBPT in any site year. Urea + NBPT + DCD was significantly lower than CAN in one site year with no differences in the other site years.

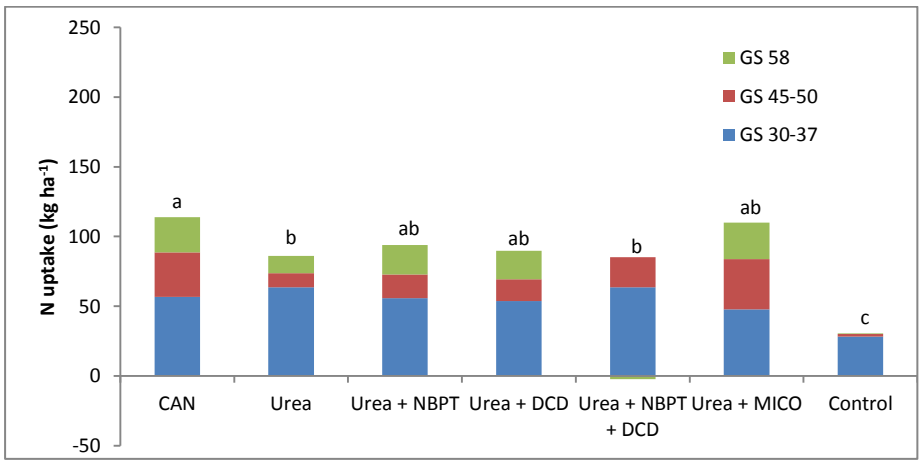
Table 7.4 Significant effects of N fertiliser formulation and site year x crop GS and their interaction on in season crop N uptake

Effect	**In season N Uptake**
	P value
Site year * Crop GS	<0.0001
N fertiliser formulation	<0.0001
Site year * Crop GS * N fertiliser formulation	0.0298

(a)



(b)



(c)

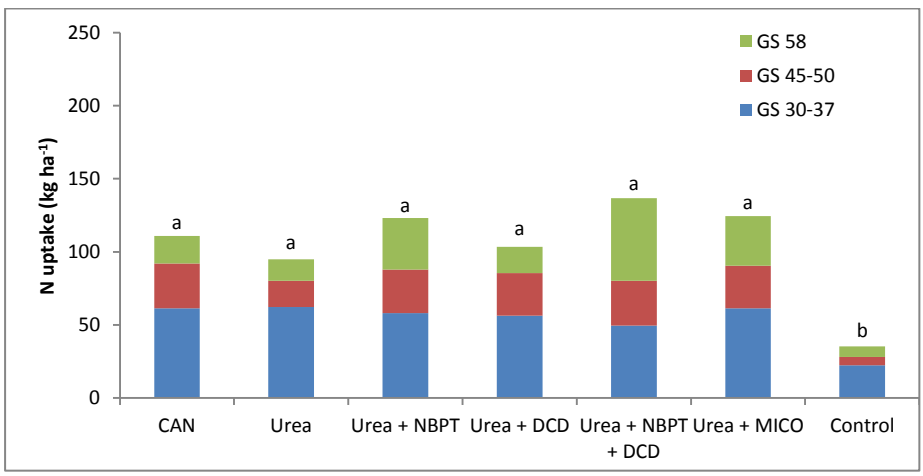


Figure 7.5 In season N uptake across three growth stages for experiment 2. (a) JC 2014, (b) MT 2014 and (c) MT 2015

*Different letters represent significant differences between N fertiliser formulations within site years using F protected LSD test (P<0.05) for GS58

7.4.4.1 Grain Yield

There was a significant site year by N fertiliser formulation interaction on grain yield ($P<0.001$) for the larger number of N fertiliser formulations evaluated in dataset 2 (Table 7.5). All fertiliser formulations produced higher grain yield than the unfertilised control (Table 7.6) and fertiliser formulations were not significantly different to each other except for JC 2014 where urea + NBPT was significantly higher than urea + MICO (Table 7.6). The JC site produced higher grain yield than MT by approximately 1.5 – 2 t ha^{-1}. On average CAN produced the highest grain yield numerically with 8.54 t ha^{-1}. The CAN relative yield was 98% for urea, 100% for urea + NBPT and 95% for urea + DCD, urea + NBPT + DCD and urea + MICO.

Table 7.5 Significant effects of N fertiliser formulation and site year and their interaction on grain yield, total crop N uptake and protein percentage across three site years (MT 2014, 2015 and JC 2014)

Effect	**Grain Yield**	**Total N Uptake**	**Protein %**
N fertiliser formulation	<0.0001	<0.0001	0.2453
Site year	<0.0001	<0.0001	<0.0001
N fertiliser formulation* site year	<0.0001	0.2087	0.3965

Table 7.6 Grain yield as affected by N fertiliser formulation in experiment 2

Treatment	JC 2014	MT 2014	MT 2015	Average	CRY
		Grain Yield (t ha^{-1})			
CAN	9.77 ab	7.72 a	8.14 a	8.54	100%
Urea	9.44 ab	7.70 a	8.07 a	8.40	98%
Urea + NBPT	10.15 a	7.66 a	7.79 a	8.53	100%
Urea + DCD	9.56 ab	7.05 a	7.77 a	8.13	95%
Urea + NBPT + DCD	9.38 ab	7.06 a	7.79 a	8.08	95%
Urea + MICO	9.16 b	7.38 a	7.75 a	8.10	95%
Control	8.19 c	2.68 b	3.12 b	4.66	

*pooled standard error ranged from 0.29 –0.32

*Different letters represent significant differences between N fertiliser formulations using F protected LSD test (P<0.05)

*CRY = CAN relative yield

7.4.4.2 Total N Uptake

There was no significant two way interaction for total crop N uptake between N fertiliser formulation and site year (P<0.05) but there was a significant N fertiliser formulation effect and a site effect (P<0.05) (Table 7.5). All fertiliser formulations were significantly higher than the unfertilised control (Figure 7.6). CAN was significantly higher than urea with 148.93 kg N ha^{-1} compared to 131.36 kg N ha^{-1} from urea. Total N uptake from urea + NBPT was not different to CAN and CAN was significantly higher than urea + MICO.

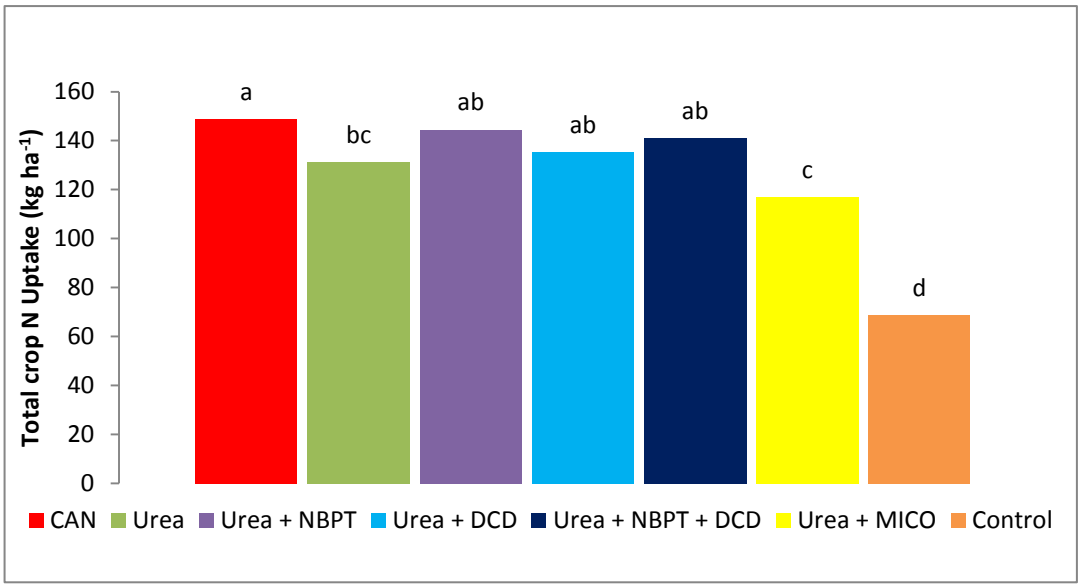


Figure 7.6 Total crop N uptake for different N fertiliser formulations in experiment 2

*Different letters represent significant differences between N fertiliser formulations using F protected LSD test (P<0.05)

7.4.4.3 Grain protein percentage

There was no significant two way interaction for protein between N fertiliser formulation and site year (P>0.05) and there was also no significant N fertiliser formulation effect on grain protein percentage (P>0.05) and so the average grain protein percentage for dataset 2 was 9.25%. The N fertiliser formulation grain protein percentages are shown in Figure 7.7.

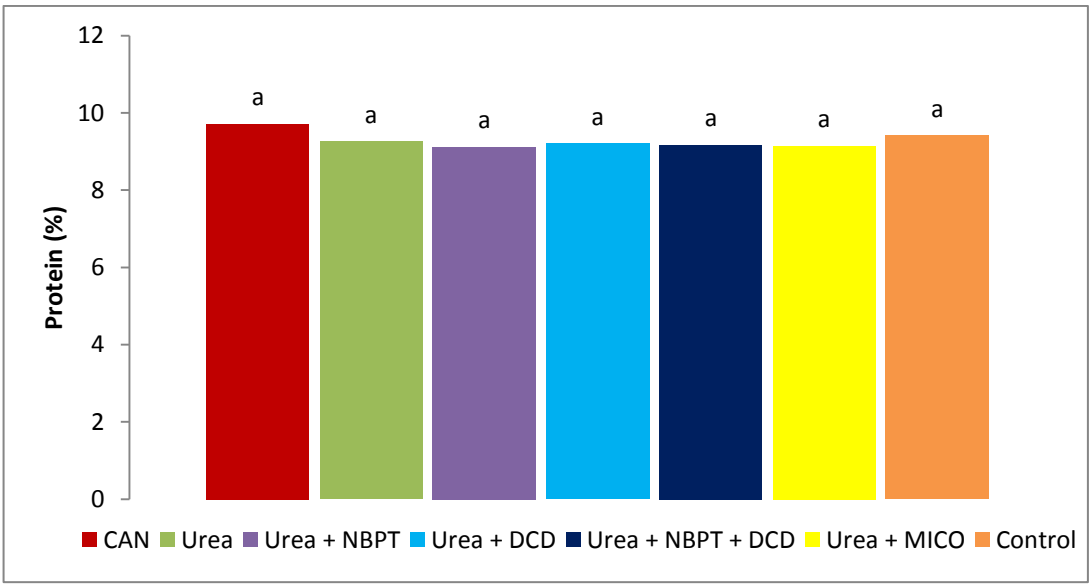


Figure 7.7 Grain protein percentage for different N fertiliser formulations in experiment 2

7.5 Discussion

7.5.1 In Season N uptake

The in season N uptake samples for MT in 2014 and 2015 showed that by GS 30 – 37, between 47 and 64 kg N ha^{-1} was taken up by the crop, by GS 45 – 50, between 70 and 92 kg N ha^{-1} was taken up by the crop and by GS 58, between 83 and 125 kg N ha^{-1} was taken up by the crop. This is in agreement with the Teagasc Spring barley guide where it shows that by GS 59 approximately 131 kg N ha^{-1} is taken up by the crop (Teagasc, 2016b). At JC 2014, crop N uptake was higher with values ranging from 70 to 115 kg N ha^{-1} at GS 30 - 37, 110 to 198 kg N ha^{-1} at GS 45 - 50 and 165 to 213 kg N ha^{-1} at GS58. The unfertilised control at JC 2014 had higher N uptake than any of the controls in the other site years with 114 kg N ha^{-1} at GS 58 compared to 60 kg N ha^{-1} in JC 2015, 31 kg N ha^{-1} in MT 2014 and 35 kg N ha^{-1} in MT 2015. As mentioned in the materials and methods in section 3.3.1 this site had received high quantities of organic manure when it was cropped with grassland and maize and may have had higher N mineralisation rates during the growing season supplying extra N to plants as well as N fertiliser applied. Schroder et al. (2007) showed that dry matter and N yields responded positively to manure applications from previous years in a cut grassland crop and Whitmore and Schroder (1996) estimated that a build-up of organic manure applications can lead to an extra 70 kg N mineralised ha^{-1} $year^{-1}$. JC 2014 had between 54 – 83 kg N ha^{-1} higher N uptake in the control plot compared to MT 2014 and 2015 indicating that there were higher N mineralisation levels at this site compared to MT due to the background mineralisation rates.

The N index system in Ireland accounts for a build-up of organic manure from previous applications and previous cropping history (Coulter and Lalor, 2008) which would mean that the maximum N application rate for JC is 120 kg N ha^{-1} (index 2 with 8.5 t ha^{-1} crop) versus a 155 kg N ha^{-1} at MT (index 1 with 8.5 t ha^{-1} crop).

Differences between fertiliser formulations for in season N uptake were not consistent as the results were variable from year to year. In MT 2014 CAN was significantly higher than urea at GS58 but showed no differences in JC 2014 or MT 2015 highlighting the variability of using urea in different years. CAN was significantly higher than urea + NBPT + DCD and urea + MICO at GS 30 - 37, urea + NBPT + DCD, urea + MICO and urea + NBPT at GS 45 - 50 and by GS 58 there were no differences between the fertiliser formulations.

7.5.2 Effect of urea compared to CAN on grain yield and N uptake

Nitrogen fertiliser applied as CAN and urea produced similar yields in all site years which was surprising as many studies have shown yield reductions, at least in some site years, using urea compared to CAN (Devine and Holmes 1963a; Gately 1994; Bhogul et al., 2003). Application of urea to the seedbed in close proximity to the seed can cause seedling damage due to ammonia toxicity and can contribute to reduced yields. The fertiliser in this study was surface broadcast so seed toxicity did not take place. The weather at the time of N application was dry and according to Terman (1979) in Bhogul et al. (2003) urea applied to air-dry soil does not hydrolyse and if a large amount of rain falls after application, this can wash urea into the soil and minimise ammonia emissions. Holocomb et al. (2011) reported that 14.6 mm irrigation immediately following urea application reduced NH_3 losses by 90% and Sanz-Cobena et al. (2011) reported that the addition of 7mm of water reduced NH_3 emissions by 77% and the addition of 14mm of water reduced NH_3 emissions by 89%. Forrestal et al. (2015) reported that 5.8mm precipitation resulted in 8% loss of N as NH_3 which was much lower than the average of 25.1% loss at the same site. In the current study the main application of concern was the second split fertiliser application of 120 kg N ha^{-1} and in JC 2013 and 2014 and MT 2013 there was less than 5mm rainfall

after application with most of the rainfall occurring after 6-15 days. Because the N fertiliser was applied to dry soil the urea hydrolysis levels were likely to be low and so minimal NH_3 losses may have occurred which resulted in similar yields between CAN and urea. It is also important to consider N uptake, as the uptake of N could be different between fertiliser types even though yields are similar. Urea had significantly lower N uptake levels than CAN which is in agreement with previous studies (Devine and Holmes 1963b). So although yields were similar between CAN and urea, differences were detected in N uptake levels.

7.5.3 Effect of N stabilisers on grain yield and N uptake

The addition of N stabilisers to soils did not have any effect on grain yield compared to CAN or urea in this study. The only significant difference observed was at JC 2014 where urea + NBPT was significantly higher than urea + MICO. Studies have shown that urea + MICO is not an effective urease or nitrification inhibitor (Chien et al., 2014; Franzen et al., 2011; Goos et al., 2013) and Chien et al. (2014) concluded that it should not be recommended to farmers for improving nitrogen use efficiency. The meta analysis of Abalos et al. (2014) showed that the use of N stabilisers increased crop yield on average by 7.5% out of 27 studies. The addition of NBPT to urea had no significant effect on grain yield which is in agreement with Abalos et al. (2012). The addition of DCD in this study did not have any significant effects on yields. The literature shows contrasting results with some studies showing no significant effect of DCD on yields (Misselbrook et al., 2014; Abalos et al., 2016), some studies indicating yield increases (Liu et al., 2013; Abalos et al., 2014) while other studies show yield decreases (Hinton et al., 2015). Yield decreases can generally be explained by NH_3 emissions as when DCD is applied to soil, NH_4^+ remains in the soil for longer along with a prolonged spike in pH by urea hydrolysis thereby

increasing NH_3 emissions (Forrestal et al., 2015). The addition of NBPT to urea increased N recovery to similar levels to CAN indicating that it reduced NH_3 losses compared to urea alone. The addition of DCD to urea had no effect on yield compared to using urea alone. Urea + MICO was significantly lower than all fertiliser formulations except for urea and as stated above, previous studies have shown this to be an ineffective urease and nitrification inhibitor. Using urea + NBPT maintained similar yield and N uptake to CAN which is in agreement with other studies that showed reduced NH_3 emissions using NBPT (Watson et al., 1990b; Forrestal et al., 2015). Using NBPT has also been shown to reduce N_2O emissions compared to CAN (Roche et al., 2016) and all of these results together show that using urea + NBPT in place of CAN is a viable option for Irish tillage farmers.

7.5.4 Effect of site year on yield

In both datasets there was a significant N fertiliser formulation x site year effect. Grain yield from the unfertilised control plots at JC were much higher than MT in both years. As explained in section 3.3.1 and also discussed in 3.5.1 this site received annual applications of organic manure when cropped with grassland and maize. Schroder et al. (2007) showed that repeated organic manure applications can have positive effects on N supply in future years due to delayed N mineralisation of organic manure fractions which explains the higher yield from control plots at JC compared to MT. The in season N uptake data also showed higher N uptake rates from control plots in JC compared to MT which indicates that higher N mineralisation rates from background organic matter was taking place. Macronutrients were applied to both sites in sufficient quantities at the beginning of each year to ensure that these would not affect the study results. The soil characteristics shown in table 3.1 in chapter 3 show that levels of P and K were similar at both sites and that pH

levels were also similar indicating that these had no effect on the higher yields observed at JC and that the organic manure history at JC can explain these higher yields.

7.5.5 Effect of N fertiliser type on grain protein levels

There was no effect of N fertiliser formulation x site year on grain protein concentration but there was a treatment effect in experiment 1 and a site year effect in both experiments. Hackett (2014) showed that grain protein content is quite variable between sites and seasons, which was observed in the current study, and concluded that it is difficult to achieve an optimum protein range for malting barley consistently. Protein levels were only below the malting threshold at MT 2015 with 8.27% in experiment and 8.35% in experiment 2. All other site years were within the malting barley specification of between 8.8% and 10.8%. For experiment 1 there was a significant N fertiliser formulation effect where CAN had significantly higher grain protein concentration than urea + NBPT and urea + DCD but all N fertiliser formulations were within the malting specification of 8.8% - 10.8% and would be accepted for malting purposes. The protein content of CAN was significantly higher than urea + NBPT in experiment and the crop N uptake for CAN and urea + NBPT were similar. Grain yields within experiment were higher for urea + NBPT compared to CAN in three out of five site years with grain yield increases ranging from 0.04 t ha^{-1} to 0.40 t ha^{-1}. The lower protein content with urea + NBPT can be explained by a dilution effect of the protein content by the extra grain yield. Overall, switching from CAN to a urea based fertiliser formulation will not negatively affect grain protein concentrations.

7.6 Conclusions

In general, the use of N stabilisers (urease and nitrification inhibitors) did not affect grain yields compared to using CAN. Nitrogen uptake was significantly lower for urea compared to CAN indicating that N can be lost from urea as NH_3. Although yields were similar between CAN and urea in this study, there should be caution when using urea due to its variability as other studies have shown it can result in reduced yields compared to CAN. The addition of NBPT to urea increased N uptake to similar levels to CAN indicating it reduced NH_3 losses compared to urea and this would be a more viable option to protect against NH_3 losses. The grain protein content was similar regardless of the N fertiliser source used and switching N fertiliser source will produce grain protein content within the malting barley specifications. The results from this study are positive for switching from CAN to a stabilised urea formulation for spring barley production. However, as crop diversification is increasing in Ireland under new greening measures, the performance of N stabilisers on other crops including wheat, oats, oilseed rape and cover crops (catch crops) is required to assess the viability of these products on other arable crops in Ireland. In addition, inconsistent spread evenness during spreading, due to low granule density, granule shattering and generally poor ballistics, especially at large bout widths (24m) with high disc speeds may be a larger impediment to uptake in the tillage sector (Forristal 2016).

Chapter 8 - Overall Discussion and Conclusions

8.1 Overview

The aim of this chapter is to summarise the key findings from each chapter of this research thesis (chapters 4 – 7) and to integrate the results for discussion. The objective of this thesis was to assess the impact of different N fertiliser formulations on yield, fNUE and reactive N loss. We compared CAN and urea with and without N stabilisers, on environmental N losses and also grain yield and N uptake of spring malting barley in Ireland. The results are discussed in terms of switching N fertiliser source in order to reduce environmental N losses and at least maintain but potentially improve grain yield and N uptake and hence improve total sustainability. The chapter ends with further research needs in the study area and concluding remarks

8.2 Synopsis of main research findings

Chapter 1 and **chapter 2** identified the need for developing NH_3 and N_2O mitigation options from agriculture in Ireland. A review of the scientific literature summarised in **chapter 2** led on to the development of the studies in the subsequent chapters. The literature review identified that agriculture is responsible for 99% of NH_3 emissions and 33% of total GHG emissions and that this is expected to increase to 48% by the year 2020 (Duffy et al., 2015). Ireland has commitments under the EU climate and energy package to reduce GHGs by 20% below 1990 levels by 2020 and more recently has committed to reduce GHG emissions by 30% relative to 2005 levels under the climate and energy framework 2030. This means that agriculture must reduce its overall emissions. Simultaneously, the Irish government has set targets to grow agricultural output and revenue generated from this sector in its FH 2020 and FW 2025 plans. Spring barley accounts for approximately 50% of the total arable area in Ireland and the main GHG in arable systems is N_2O from the application of N fertilisers to soils. Calcium ammonium

nitrate is the dominant N fertiliser used in Ireland and contributes to N_2O emissions and NO_3^- leaching. Switching fertiliser N source from CAN to urea has potential to reduce these emissions but could increase NH_3 emissions. As a result, a holistic, multi-gas approach is required in order to provide a robust assessment of any abatement strategy. The addition of N stabilisers to urea has potential to reduce these N losses and maintain N in the soil for longer which could potentially increase yields and crop N uptake. This study investigated different N fertiliser formulations on N_2O emissions in **chapter 4**, NO_3^- leaching in **chapter 5**, NH_3 emissions in **chapter 6**, and grain yield and crop N uptake in **chapter 7**.

In **chapter 4,** N_2O emissions were measured from different N fertiliser formulations including CAN and urea with and without N stabilisers. Emission factors were generated and compared to the IPCC default value of 1%. Results showed that overall, N_2O emissions were low regardless of the N fertiliser formulation used but the addition of N stabilisers to urea could reduce N_2O emissions relative to CAN. Using the IPCC default value of 1% overestimates N_2O emissions. Approximately 133,000 hectares of spring barley is grown in Ireland (CSO, 2016) and using the 1% default EF with 150 kg N ha^{-1} applied this would amount to 199,500 kg N_2O yr^{-1}. Using the average CAN EF of 0.35% would reduce this N_2O loss to 69,825 kg N_2O yr^{-1} which is a 65% reduction compared to the default value. This highlights the importance of using more accurate EFs for estimating N_2O emissions for national inventories. Using the average EF for urea + NBPT of 0.20% would amount to 39,900 kg N_2O yr^{-1} which is a 43% reduction compared to CAN and using the average EF for urea + DCD of 0.13% would amount to 25,935 kg N_2O yr^{-1} which is a 63% reduction compared to CAN. Overall this study showed that regardless of N fertiliser formulation used N_2O emissions were much lower than IPCC default and this default EF is not appropriate for use in spring barley in Ireland. The use of N stabilisers

reduced N_2O emissions compared to CAN but indirect losses of NO_3^- leaching and NH_3 emissions must be considered as this could increase EFs. The potential of N stabilisers to reduce NO_3^--N leaching was studied in **chapter 5**. Nitrate leaching was measured from CAN, urea and urea + NBPT + DCD over a two year period and showed no differences between fertiliser formulations and these results indicate that similar emission factors should be applied to CAN, urea and urea + NBPT + DCD for indirect emissions of N_2O from leached NO_3^-. This means that switching N fertiliser source from CAN to urea with N stabilisers can reduce N_2O emissions and will not have a negative impact on NO_3^- leaching to water bodies. Indirect N_2O emissions associated with NH_3 emissions must also be considered. In **chapter 6**, NH_3 concentrations were measured from CAN, urea and urea + NBPT. The results in this chapter were a relative comparison and were not quantified but showed significant reductions in NH_3 concentrations using urea + NBPT compared to urea. Ammonia concentrations from CAN and urea + NBPT were similar. These results indicate that similar emission factors should be applied to CAN and urea + NBPT for indirect emissions of N_2O from NH_3 losses but that a higher EF would be needed for urea. If indirect EFs for NH_3 loss were applied to the different N fertiliser formulations, they would increase the overall EF for urea. However CAN and urea + NBPT would have similar EFs for this indirect emission pathway. Urea + DCD was not assessed in this study but other studies have shown increased NH_3 emissions similar to urea (Forrestal et al., 2015) which would increase the EF for urea + DCD similar to CAN. Switching N fertiliser source has potential to reduce gaseous losses of N but with projected production targets under FW 2025 this must not negatively impact yields or N uptake. Spring barley grain yields, N uptake and protein percentage were studied in **chapter 7**. There were no differences between the different N fertiliser formulations on spring barley grain yield in any year except for urea + MICO which had significantly lower grain yield than urea +

NBPT in one site year. There were significant differences in N uptake with lower N uptake from urea, urea + DCD and urea + MICO compared to CAN. Using urea + NBPT gave consistently similar N uptake levels to CAN.

Overall this study shows that using urea + NBPT can reduce N_2O emissions compared with CAN from spring barley with no negative impact to NH_3 emissions, NO_3^- leaching or grain yield or grain quality.

8.3 Overall implications of this research

8.3.1 Impact on National Inventory

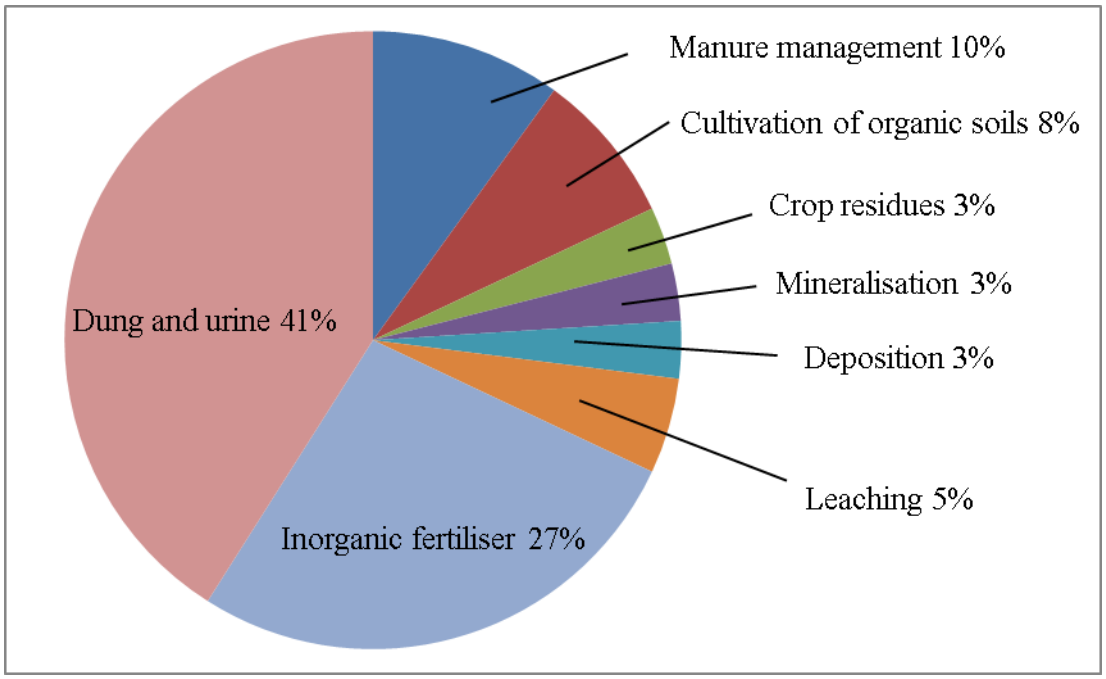
This research calculated N_2O EFs for a suite of N fertiliser formulations on a typical spring barley soil type in Ireland. This is an important step for switching from using a Tier 1 methodology to using a Tier 2 methodology with a more accurate country-specific EF. Currently, N_2O emissions are estimated using a 1% default value under the Tier 1 methodology from the IPCC and estimate that 1% of applied N fertiliser is lost as N_2O emissions. This research shows that using this default EF of 1% for estimating N_2O emissions is not appropriate in spring barley systems in Ireland and it overestimates emissions. The highest EF calculated in this study was 0.49% which is less than half the IPCC default value. Moving to a Tier 2 methodology would mean using more detailed and more accurate country specific EFs (as calculated in this study) for better accounting for national emissions. Using a more accurate EF would result in reduced emissions of N_2O from spring barley and potentially other crops also. This study has also shown that using urea stabilised with the urease inhibitor NBPT in place of CAN may reduce N_2O emissions further, taking into account indirect emissions associated with NO_3^- leaching and NH_3 emissions. This research is pivotal for reducing N_2O emissions from spring barley and

potentially other crops in a temperate maritime climate like Ireland. This contributes to the overall reduction of GHG emissions from the agriculture sector helping Ireland meet GHG reduction targets and comply with governmental legislation including the climate and energy framework 2030.

Similar research studies comparing the same suite of N fertilisers on grassland and generating EFs have been conducted in Ireland (Harty et al., 2016a) as well as disaggregated EFs for dung and urine on grassland (Krol et al., 2016). These figures combined with the figures from this research have been used to generate an estimate of the effect of switching from the Tier 1 default value of 1% to the generated EFs using Tier 2 (Lanigan,G.J. 2016). Using the Tier 2 generated EFs and recalculating the N_2O inventory would change the 2014 emissions data as follows:

- The contribution of dung and urine deposits to the total emissions would reduce from 41% to 23% (Figure 8.1)
- The contribution of mineral N fertiliser to the total emissions would increase from 27% to 38% (Figure 8.1)
- Switching the method from using the default value of 1% in Tier 1 to the more accurate measured EFs for Tier 2 would reduce the total GHG emissions of 58.25 MT CO_2 eq in 2014 by 1.01 Mt CO_2 eq. The impact of this from the period of 1989 to 2014 can be seen in figure 8.2.

(a)Tier 1



(b) Tier 2

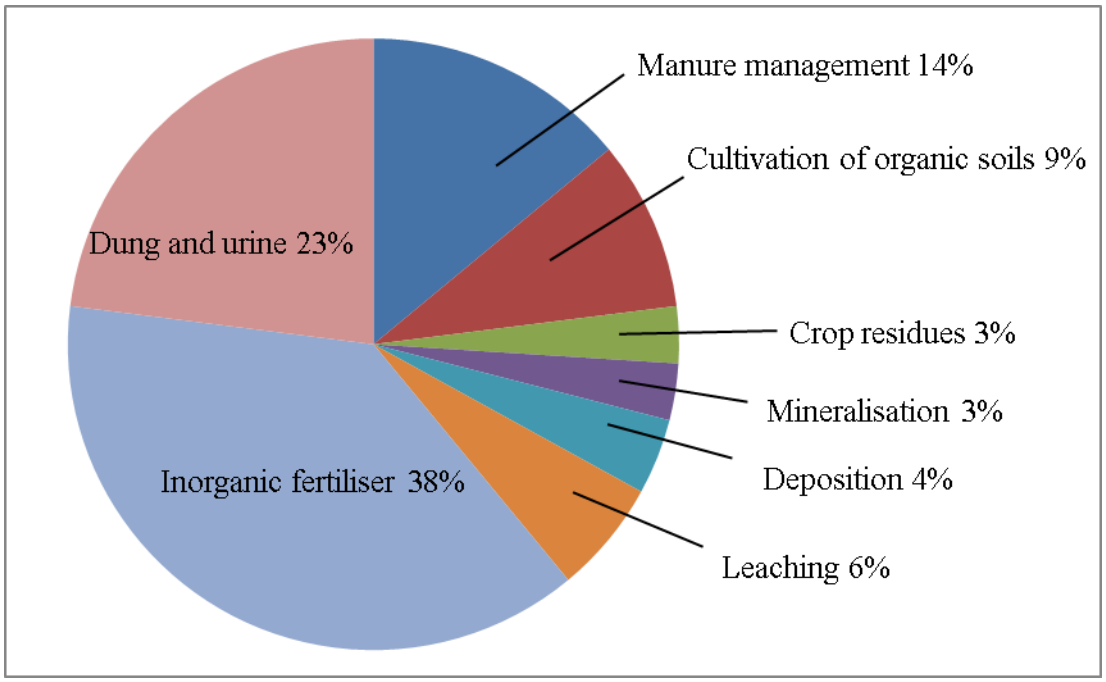


Figure 8.1 Impact of Switching from Tier 1 (a) to Tier 2 (b) methodology on N_2O emissions (Lanigan, G.J. 2016)

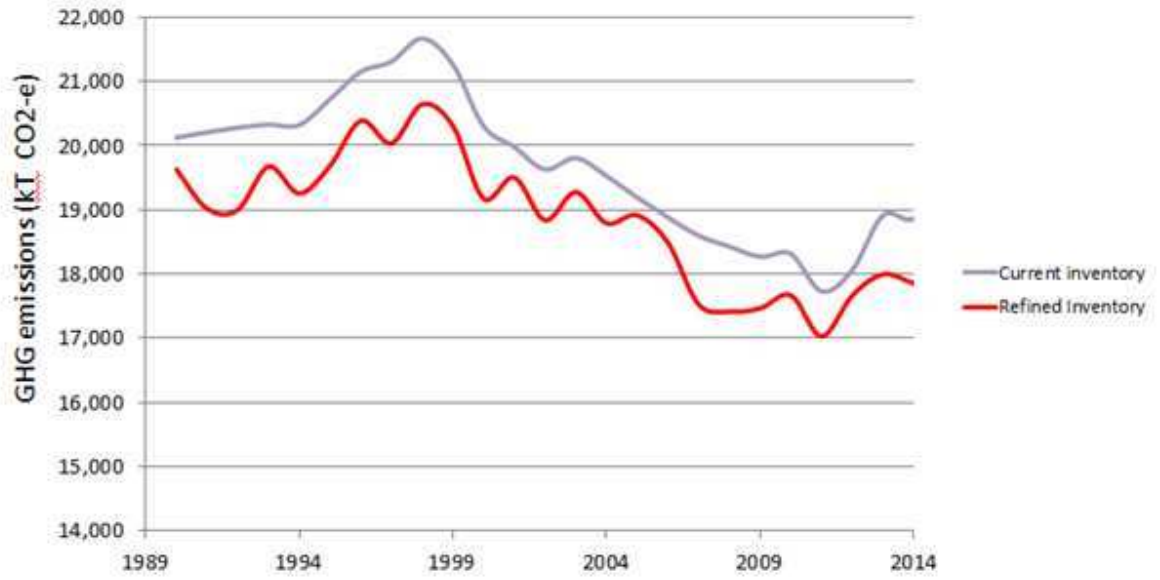


Figure 8.2. Impact of switching from Tier 1 to Tier 2 methodology on N_2O emissions profile from 1989 – 2014 (Lanigan, G.J. 2016)

Using a Tier 2 methodology changes the contribution of emissions within different sectors and the contribution of emissions from chemical fertilisers increased from 27% to 38%. However, with this research combined with the research in Harty et al, 2016a, switching N fertiliser source is a mitigation option for reducing these emissions. Switching 45% of CAN to a stabilised urea product would result in a reduction of 0.77 million tonnes of CO_2 eq from chemical fertilisers (Lanigan, G.J., 2016). In order to achieve these reductions, it is necessary for farmers to switch from using the traditional CAN to using the stabilised urea, urea + NBPT. The impact of urea + NBPT on grain yield is important as there are also production targets in Ireland under FW2025 and this may also be a deciding factor for farmers to switch N fertiliser source.

8.3.2 Impact on national policy – Food Wise 2025

On the flip side of reducing environmental N losses, there are national production targets in Ireland under FW 2025 to increase the value of primary production by 65%. On a global scale, the world's population is increasing and so, more crops will be required to feed this growing population which inevitably means more N fertiliser use. This study showed no significant differences between fertiliser formulations for grain yield, however, urea + NBPT did produce up to 0.4 t ha^{-1} more grain yield than CAN, on occasion, so there is potential for increased grain yields by switching N fertiliser source but further research is required. A similar research study comparing N fertiliser formulations on grassland in Ireland also showed CAN and urea + NBPT to have similar yields (Harty et al., 2016b). Overall, this research shows that switching from CAN to urea + NBPT will produce similar yields in both grassland and spring barley while reducing N_2O emissions. However, there are economic and practical considerations of switching from CAN to stabilised urea.

8.3.3 Economic considerations of switching from CAN to stabilised urea

Stabilised urea products became available on the market in Ireland in 2014 and at the time were at a 5% lower cost than CAN per unit of N. Fertiliser prices have fluctuated since and both CAN and stabilised urea are currently at a similar cost. Stabilised urea (Urea + NBPT) can provide environmental benefits as shown in this study as well as equivalent agronomic performance to CAN but in order for farmers to switch fertiliser formulations it may be necessary to provide incentives. Currently, switching from CAN to urea + NBPT costs the same but switching from CAN to urea provides the farmer with a cost saving of approximately €0.20 per kg N (David Wall, personal communication). This study showed that similar yields are achieved using CAN and urea and so, on an economic basis farmers could decide to use urea instead of urea + NBPT. This would lead to increases in NH_3

emissions which would indirectly contribute to N_2O emissions. It may be necessary to provide incentives for farmers to choose urea + NBPT over urea which would be the best option environmentally and would provide farmers with protection against NH_3 losses and maintain yield and N uptake. Sales of CAN per t of N have been declining over the last few years and sales of urea have been increasing (Table 8.1). Sales of urea + NBPT began in 2014 and have been increasing over the last few years but at much lower levels than CAN and urea sales (Table 8.1).

Table 8.1 CAN, urea and urea + NBPT sales in Ireland from 2012-2016

	CAN (t of N)	**Urea (t of N)**	**Urea + NBPT (t of N)**
2012	136,006	29,075	
2013	148,901	29,538	
2014	137,199	34,187	773
2015	128,666	37,925	2,320
2016	124,866	47,542	5,637

*Sales of urea and CAN (John Corr, personal communication

*sales of urea + NBPT (Brett Wesley, personal communication)

Fertiliser cost is one of the barriers to farmer uptake of urea + NBPT (Brett Wesley, personal communication) and it may be necessary to provide a cost incentive to encourage farmers to switch. There are also practical considerations of switching N fertiliser source to urea + NBPT.

8.3.4 Practical considerations of switching from CAN to stabilised urea

Switching from CAN to urea + NBPT would have implications for famers for spreading fertiliser precisely, as urea has a lower density than CAN (Forristal, 2016). Spreaders have increasing sized bout widths which pose challenges for farmers for spreading fertiliser accurately. Careful selection of urea products with good physical characteristics and correctly calibrating the fertiliser spreader is required to ensure an even spread (Forristal, 2016). The spread ability of urea is another barrier to farmer uptake (Brett Wesley, personal communication), particularly with tillage farmers as they fear that urea wont spread at wider bout widths of 24m and above. Grassland farmers are less concerned with bout widths and so the spread ability issue is just with tillage farmers. The spreadability of urea + NBPT has not been a problem as the urea that fertiliser companies use is of a high grade consistent urea with a good crush strength of 5-7 kg and a uniform granule size (Brett Wesley, personal communication). There are other barriers to farmer uptake as well as cost and the spread ability of urea which are as follows (Brett Wesley, personal communication):

- Farmers have used urea in the past and it didn't work well for them so they have no confidence in urea products.
- CAN works so why change? Financial savings not good enough.
- Impact on pH, using urea products increases pH and therefore more lime may be required. This is generally no more quickly than the effect of leaching from the Irish wet climate.

Taking these barriers to farmer uptake into account it may be necessary to provide government incentives for farmers to switch from CAN to urea + NBPT and reduce N_2O

emissions from chemical fertilisers thereby contributing to a reduction in GHG emissions from agriculture.

8.4 Conclusions

Overall, the results from this thesis show that there is scope for switching N fertiliser source from CAN to urea based formulations in tillage systems in Ireland. This is a pivotal step for arable agriculture in Ireland as CAN has been the dominant N fertiliser for many years. This study has shown that using urea in place of CAN produces the same yields but with lower N uptake and can lose N through NH_3 volatilisation. Although reduced yields were not observed in this study, other studies have observed reduced yields using urea compared to CAN showing that urea can produce variable results. Using urea + NBPT protects against this NH_3 loss and produces the same yield and N uptake as CAN and has similar NH_3 emissions as CAN with lower N_2O emissions.

These results show that by switching N fertiliser source from CAN to stabilised urea is a win-win strategy for both environmental and production targets in Ireland but further research is required to assess these fertiliser N formulations in different climatic conditions with different crops and on different soil types to ensure the consistency across these different farming scenarios.

8.5 Future Research Needs

This research has identified the need for switching N fertiliser source to reduce gaseous emissions from spring barley in Ireland and has shown that the IPCC default value of 1% is not appropriate as it overestimates N_2O emissions. With crop diversification increasing in

Ireland, further research is required on the effect of N stabilisers at reducing N_2O emissions on different crops, particularly winter crops, on different soil types and in different climatic conditions to assess if the default value of 1% is appropriate in other tillage systems. The use of N stabilisers reduced N_2O emissions in this study but results were variable between years with significant differences in one site year and not in the other. Further field trials over a longer time period and on more experimental field sites would help to identify the effect of N stabilisers in different climatic conditions and to assess if they are a viable option for other tillage crops and on other soil types.

Ammonia emissions measured in this study were a relative comparison between treatments but quantitative results are needed to assess the effect of N stabilisers on emissions and to quantify the reduction potential of urea + NBPT. Using integrated horizontal flux technique would allow the quantification of NH_3 emissions from different N fertiliser formulations. This would require larger field sites which was not possible in the current study, and would allow quantitative analysis of NH_3 emissions to better understand the effect of N stabilisers on NH_3 emissions.

Nitrate leaching was measured from CAN, urea and urea + NBPT + DCD and showed no differences between fertiliser treatments. As the results from this study indicate the potential for switching from CAN to urea + NBPT, the effect of urea + NBPT on NO_3^- leaching should be studied.

Currently there are many products on the market that claim to stabilise N fertilisers by various modes of action, some of which were evaluated in the current study. Research is required on each product to assess the effect of these new products on environmental losses and grain yield and uptake to assess if they have the same effects as urea + NBPT and urea

+ DCD and to assess if these products are effective and viable options for use in agriculture.

8.6 Concluding Remarks

There is a need to move from the current Tier 1 approach to the Tier 2 approach for estimating N_2O emissions in Ireland. This study has shown that the default value overestimates emissions and is not appropriate for use in spring barley in Ireland. Further research is needed to assess this default value on other soil types and crop types to assess the appropriateness of the 1% default value in other cropping systems.

Switching from CAN to urea + NBPT is a sustainable mitigation strategy for reducing environmental losses of N while maintaining yields in spring barley in Ireland. Although further research is required to assess the effects of N stabilisers on other crops and soil types, this is a pivotal step in developing a mitigation strategy for reducing GHG emissions from agriculture.

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Appendix

Appendix A – List of publication and presentations

2016

- Roche, L., Forrestal, P.J., Lanigan, G.J., Richards, K.G., Shaw, L.J. and Wall, D.P., 2016. Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley. Agriculture, Ecosystems & Environment, 233, pp.229-237 (publication).
- Roche, L., Forrestal, P.J., Hackett, R., Lanigan, G.J., Richards, K.G., Shaw, L.J., Wall, D.P., 2016. How does urea and protected urea compare to CAN for spring barley production. National Soil Fertility Conference, Kilkenny 2016. Efficient fertilizer use for tillage crops pp 10 – 11 (oral presentation).
- Roche, L., Lanigan, G.J., Richards, K.G., Wall, D.P. 2016. Nitrogen fertilizer selection for cereal crops – balancing agronomic and environmental goals. TResearch Spring Issue. Volume 11, Number 1, Spring 2016 pp 8 – 9 ISSN 1649 – 8917 (publication).
- Forrestal, P.J., Wall, D.P., Carolan, R., Harty, M., Roche, L., Krol, D., Watson, C.J., Lanigan, G.J. and Richards, K.G., 2016. Effects of urease and nitrification inhibitors on yields and emissions in grassland and spring barley. International Fertiliser Society, December 2016 (publication).

2015

- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Gooding, M.J., Shaw, L.J., Hackett, R., Wall, D.P., 2015. Effect of nitrogen source and inhibitors on spring barley grain yield. ASA, CSSA and SSSA International annual meeting, Minneapolis 16th – 19th November 2015 (poster presentation).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Gooding, M.J., Shaw, L.J., Hackett, R., Wall, D.P., 2015. Effect of nitrogen source on nitrous oxide emissions in spring barley. ASA, CSSA and SSSA International annual meeting, Minneapolis 16th – 19th November 2015 (Oral presentation).

- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Gooding, M.J., Shaw, L.J., Hackett, R., Wall, D.P., 2015. 45 second elevator speech contest, ASA, CSSA and SSSA International annual meeting, Minneapolis 16th – 19th November 2015 (2nd place).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Gooding, M.J., Shaw, L.J., Hackett, R., Wall, D.P., 2015. Reducing greenhouse gas emissions from Irish soils while maintaining crop production. Soil Science Society of Ireland – 'Soil Science, Diggin it' 3 minute thesis competition, (1st place for best oral presentation).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Hackett, R., Wall, D.P. 2014, 2015. Selecting nitrogen fertiliser sources for improved yield and reduced gaseous emissions in spring barley production systems, (Best overall presentation and RDS gold medal winner).
- Roche, L., Lanigan, G.J., Forrestal, P.J., Richards, K.G., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P. 2015. Effect of fertiliser nitrogen source on nitrous oxide emissions and yield in spring barley, Catchment Science, Wexford, September 2015 (poster presentation).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hacket, R., Wall, D.P., 2015. Evaluating nitrogen fertiliser source on spring barley grain yield, National Tillage Conference, Kilkenny, January 2015, (poster presentation).
- Roche, L., Lanigan, G.J., Forrestal, P.J., Richards, K.G., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P., 2015. Effect of fertiliser form on N_2O emissions from spring barley – Irish update. UK and Ireland GHG platform annual meeting, Dublin, January 2015 (oral presentation).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P., 2015. Managing the soil nitrate pool in arable systems, British soil science society early careers researcher conference (Poster presentation).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Gooding , M.J., Hackett, R., Wall, D.P., 2015. Evaluating the effect of fertiliser nitrogen type on grain yield in spring malting barley. Agricultural Research Forum, Tullamore, Co. Offaly, March 2015 (oral presentation)

- Roche, L., Lanigan, G.J., Forrestal, P.J., Richards, K.G., Shaw, L.J., Gooding, M.J., Hammond, J., Hackett, R., Wall, D.P., 2015. Investigating nitrogen source on nitrous oxide emissions and yield in spring barley, SHES research student conference annual meeting, University of Reading (oral presentation).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Hackett, R., Wall, D.P., 2015. The effect of fertiliser nitrogen source and N stabilisers on spring barley grain yield. International Fertiliser Society annual meeting, Cambridge, December 2015 (poster presentation).

2014

- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P., 2015. Evaluating nitrogen fertiliser source on spring barley. International Fertiliser Society annual meeting, Cambridge, December 2014 (poster presentation).

- Roche, L., Richards, K.G., Forrestal, P.J., Maddock, C., Hackett, R., Wall, D.P. 2014. Evaluating nitrogen fertiliser formulations for spring barley production; comparing CAN, urea and urea + N inhibitors. National tillage conference annual meeting, Kilkenny 30th January 2014. (poster presentation).
- Roche, L., Richards, K.G., Forrestal, P.J., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P. 2014. Evaluating the effect of N fertiliser type on nitrous oxide emissions from spring barley. Agricultural Research Forum, Tullamore, Co Offaly 10th & 11th March 2014 (oral presentation).
- Roche, L., Richards, K.G., Forrestal, P.J., Lanigan, G.J., Shaw, L.J., Gooding, M.J., Hackett, R., Wall, D.P. 2014. Reducing nitrous oxide emissions from spring barley in Ireland. 18th Nitrogen Workshop, Lisbon, Portugal 30th June – 3rd July 2014, (poster presentation).
- Roche, L., Forrestal, P.J., Richards, K.G., Lanigan, G.J., Gooding, M.J., Shaw, L.J., Hackett, R., Wall, D.P. 2014. Nitrous oxide emissions in spring barley production as influence by fertiliser nitrogen source and inhibitor selection. ASA, CSSA and SSSA International annual meeting, Long beach, California 2nd – 5th November 2014 (poster presentation).

2013

- Roche, L., Shaw, L.J., Gooding, M.J., Hackett, R., Richards, K.G., Wall, D.P. 2013. Fate and transport of fertiliser nitrogen under spring barley cultivation on contrasting soils. SHES Research student conference annual meeting, University of Reading 25th & 26th April 2013 (poster presentation).
- Roche, L., Richards, K.G., Forrestal, P.J., Shaw, L.J., Gooding, M.J., Maddock, C., Krol, D., Murphy, J.B., Hackett, R., Wall, D.P. 2013. Evaluating the effect of N fertiliser type on N2O emissions from spring barley. UK GHG platform annual meeting, Edinburgh 16th & 17th December 2013 (poster presentation).

Appendix B – Journal article from Chapter 4

Roche, L., Forrestal, P.J., Lanigan, G.J., Richards, K.G., Shaw, L.J. and Wall, D.P., 2016. Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley. Agriculture, Ecosystems & Environment, 233, pp.229-237.

Appendix B – Journal article from Chapter 4

Roche, L., Forrestal, P.J., Lanigan, G.J., Richards, K.G., Shaw, L.J. and Wall, D.P., 2016. Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley. Agriculture, Ecosystems & Environment, 233, pp.229-237.